

THE UNIVERSITY OF ALBERTA

A NUMERICAL MODEL FOR SIMULATING MASS TRANSPORT AND
REACTIONS DURING DIAGENESIS IN CLASTIC SEDIMENTARY BASINS

by

ALLAN S. CROWE

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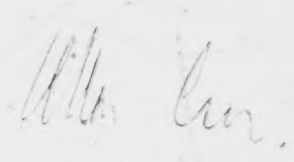
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The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled A Numerical Model for Simulating Mass Transport and Reactions during Diagenesis in Clastic Sedimentary Basins submitted by Allan S. Crowe in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A coupled mass transport and geochemical reaction model has been developed for application to numerical modelling studies of mineral stability and mass transfer in large sedimentary basins. The mass transport code is based upon a series of mixing cells formed along a stream tube. Lateral boundaries of the cells are located at a distance equal to the distance traveled due to advective transport during a time step. Thus, all mass within a cell will move to the next downstream cell at the beginning of each time step due to advection. Dispersion is incorporated into the code and acts to spread and mix the dissolved components among the mixing cells. The size, location and number of cells are determined within the program, based upon the groundwater velocities along the stream tube boundaries and a user defined time step for mass transport. Thus, calculations are undertaken for a considerably smaller area and with less computer storage and execution time requirements than a conventional distributed parameter model. Also, because much of the procedure of defining the configuration of the mixing cells is handled internally by the program, stability and convergence problems commonly associated with conventional models are minimal. The geochemical portion of the code is based on an improved version of *PHREEQE*. Specific modifications include (1) incorporation of the Pitzer equation activity coefficient model to accurately predict mass transfer among aqueous and solid phases in brines, (2) development of a technique for predicting values of the ion interaction parameters required by the Pitzer equations at temperatures from 0°C to 200°C, and (3) compilation of a data base of aqueous components, mineral equilibrium constants and virial coefficients required by the Pitzer equations, valid to 200°C.

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LIST OF SYMBOLS

- a_i = activity of a component or an ion
- a_0 = adjustable Debye-Hückel parameter related to the hydrated radius of the ion
- A = the Debye-Hückel limiting slope, which is a solvation parameter dependent upon properties of the solution
- A^ϕ = Debye-Hückel parameter for the osmotic coefficient
- b = empirical constant used to the calculation of the Debye-Hückel term for the Pitzer equations
- b_i = adjustable extended Debye-Hückel equation parameter corresponding to a specific ion and accounts for changes to the ion in very saline solutions
- B = a Debye-Hückel solvation parameter, which is a function of the properties of the solution
- B_{ca} = calculated second virial coefficient for cation-anion interactions
- B'_{ca} = calculated second virial coefficient for cation-anion interactions
- c = change of an ion interaction parameter with temperature
- C = an empirical parameter used in the Davies equation
- C = concentration of the solute
- C = Courant number
- C_{ca} = third virial coefficient for cation-anion interactions
- C_{IN} = concentration of the solute entering a mixing cell
- C_{OUT} = concentration of the solute leaving a mixing cell
- $C_{i,OUT}$ = concentration of the solute discharge from an upstream mixing cell
- $C_{i+1,IN}$ = concentration of the solute entering a downstream mixing cell
- C_i = concentration in a mixing cell during the present time step
- C_{i-1} = concentration in a mixing cell during the previous time step
- $C_{i,j}$ = concentration at a central point during the present time step
- $C_{i-1,i-1,j}$ = concentration at a downstream point during the previous time step
- $C_{i-1,i+1,j}$ = concentration at an upstream point during the previous time step
- $C_{i-1,i,j-1}$ = concentration at a downstream lateral point during the previous time step

- $C_{t-1,i,j+1}$ = concentration at an upstream lateral point during the previous time step
 $C_{0,i}$ = concentration at a contaminant source
 $C_{t,i}$ = concentration at a given point along a flow path
 C_{ca} = regression parameter defining the third virial coefficient for cation-anion interaction
 C_p^0 = heat capacity of a basic species (element) in the *PHREEQEX* data base
 D_L = longitudinal dispersion coefficient
 D_T = transversal dispersion coefficient
 D_j = dispersion coefficients in the coordinate directions
 E = an equivalent concentration
 $f(I)$ = term related to the ionic strength of the solution and accounts for long-range electrostatic effects (Debye-Hückel term in the virial expansion of the excess Gibbs free energy)
 $f'(I)$ = term related to the ionic strength of the solution and accounts for long-range electrostatic effects (Debye-Hückel term in the Pitzer equations)
 $g(x)$ = empirical function based upon the ionic strength of a solution for the Pitzer equations
 $g'(x)$ = empirical function based upon the ionic strength of a solution for the Pitzer equations
 G_i = Gibbs free energy of component i
 $G_{f,i}$ = Gibbs free energy of formation from the elements of component i
 G_i^0 = Gibbs free energy of component i at standard state
 $G_{f,i}^0$ = Gibbs free energy of formation from the elements of component i at standard state
 G_j = Gibbs free energy of the product components
 G_j^0 = Gibbs free energy of the product components at standard state
 $G_{f,j}^0$ = Gibbs free energy of formation from the elements of component j at standard state
 G_k = Gibbs free energy of the reactant components
 G_k^0 = Gibbs free energy of the reactant components at standard state

- $G_{f,k}^0$ = Gibbs free energy of formation from the elements of component k at standard state
 G_R^0 = Gibbs free energy of the reaction at standard state
 G^{ex} = excess Gibbs free energy
 G^{ideal} = Gibbs free energy of an ideal system
 G^{real} = Gibbs free energy of a real system
 I = ionic strength
 K_{xx} = horizontal component of hydraulic conductivity
 K_{yy} = vertical component of hydraulic conductivity
 K_{eq} = the equilibrium constant
 m_a = molality of an anion
 m_c = molality of a cation
 m_n = molality of a neutral species
 m_i = molality of an aqueous component or an ion
 n_c = number of mixing cells within a stream tube
 n_w = number of kilograms of solvent
 P = Peclet number
 $\hat{P}$ = mixing cell Peclet number
 q = specific discharge
 R_i = chemical reactions applied to the solute
 R = gas constant
 $R(\zeta_n)$ = reactions of mass transfer between minerals and dissolved components in a mixing cell
 s = distance along a flow path at which concentration is calculated
 S^0 = entropy of a basic species (element) in the *PHREEQEX* data base
 t = time
 t_l = total transit time along the lower stream line which bounds a stream tube
 t_u = total transit time along the upper stream line which bounds a stream tube

- T = temperature of interest
 T_R = reference temperature (298.15K)
 v = average linear groundwater velocity
 v_i = average linear groundwater velocity in the coordinate directions
 v_L = groundwater velocity parallel to the direction of flow
 v_x = horizontal component of the groundwater velocity
 v_y = vertical component of the groundwater velocity
 V = volume of a mixing cell
 $V_{i,OUT}$ = volume of groundwater flowing out of an upstream mixing cell
 $V_{i+1,IN}$ = volume of groundwater flowing into a downstream mixing cell
 V_{IN} = volume of groundwater flowing into a mixing cell
 V_{OUT} = volume of groundwater flowing out of a mixing cell
 V'_{OUT} = volume of groundwater discharged from a mixing cell before mixing occurs
 x = horizontal coordinate direction
 y = vertical coordinate direction
 Y = ion interaction parameters for the Pitzer equations
 $Y(T)$ = ion interaction parameters for the Pitzer equations at the temperature of interest
 $Y(T_R)$ = ion interaction parameters for the Pitzer equations at 25°C
 z_i = charge of an ion
 z_a = charge of an anion
 z_c = charge of a cation
 ϵ_L = longitudinal dispersivity
 $B_{ca}^{(0)}$ = regression parameters defining the second virial coefficients for cation-anion ion interaction in 1:1, 1:2, 2:1, etc. electrolytes
 $B_{ca}^{(1)}$ = regression parameters defining the second virial coefficients for cation-anion ion interaction in 1:1, 1:2, 2:1, etc. electrolytes
 $B_{ca}^{(2)}$ = regression parameters defining the second virial coefficients for cation-anion ion interaction in 2:2 and higher electrolytes

- γ_i = activity coefficient of an aqueous component or an ion
 γ_M = activity coefficient of a cation
 γ_N = activity coefficient of a neutral species
 γ_X = activity coefficient of an anion
 γ_{MX} = activity coefficient of an electrolyte
 Γ = parameter describing the degree of mixing within a mixing cell
 $\zeta_{i,tot}$ = total mass of element i within the system
 $\zeta_{i,(aq)}$ = mass of an aqueous species containing element i
 $\zeta_{i,(s)}$ = mass of a solid phase containing element i
 $\zeta_{i,(g)}$ = mass of element i present as a gas
 ζ_t = mass within a cell during the present time step
 ζ_{t-1} = mass within a cell during the previous time step
 ζ_{IN} = amount of mass entering a mixing cell
 ζ_{OUT} = amount of mass leaving a mixing cell
 ζ_{in} = mass introduced into a mixing cell by advection at the start of a time step
 ζ_d = mass remaining in a mixing cell following dispersion
 ζ_{ad} = new mass in a mixing cell following advection, dispersion or reaction
 ζ_r = mass in a mixing cell following reactions between the mineral phases
 ζ_{disp} = mass transfer among mixing cells due to dispersion
 ζ_{reac} = mass transfer between solids and aqueous phases within a mixing cell due to reactions
 θ = porosity
 Θ = second virial coefficient accounting for short-range interaction between ion pairs of like charge signs in electrolyte mixtures
 Θ_{ij} = coefficient for short-range interaction between ions of like signs
 Θ'_{ij} = coefficient for short-range interaction between ions of like signs
 $E_{\Theta_{ij}}(\eta)$ = electrostatic function for ion interaction between ions of like signs
 $E_{\Theta'_{ij}}(\eta)$ = electrostatic function for ion interaction between ions of like signs

- λ = second virial coefficient accounting for ion interaction between neutral species and ions
 $\lambda_{ij}(I)$ = term to account for short range interaction between ion pairs
 μ_{ijk} = term to account for triple ion interaction at high ionic strengths
 v = total number of ions in the chemical formula of an pair
 v_M = number of cations in the chemical formula of an ion pair
 v_X = number of anions in the chemical formula of an ion pair
 ξ_L = longitudinal advective delay parameter
 ϕ = hydraulic potential
 χ_L = longitudinal dispersive delay parameter
 χ_T = transversal dispersive delay parameter
 $\hat{\chi}$ = lumped parameter dispersive factor for a mixing cell
 ψ = third virial coefficient accounting for triple ion interactions in electrolytes
 Ψ = stream function value
 Δl = width of a mixing cell parallel to the direction of flow
 Δl_i = grid spacing in the coordinate directions
 Δp = perpendicular distance across a stream tube
 Δs = distance along a stream line traveled during a time step
 Δt = size of the time step
 Δx = horizontal distance between points or nodes
 Δy = vertical distance between points or nodes
 $\Delta \zeta$ = difference in mass in a mixing cell due to reactions and dispersion
 $\Delta \Psi$ = change in the stream function value across a stream tube
 ΔH_R° = enthalpy of the mineral dissociation or species association reaction at 25°C
 ΔH_f° = enthalpy of formation of a mineral or a species at 25°C
 ΔG_f° = free energy of formation of a mineral or a species at 25°C

I. INTRODUCTION

Most of the current concepts that link clastic diagenesis to fluid chemistry are qualitative studies, which are based upon field and laboratory oriented research. These conceptual models provide an essential framework from which we can build an understanding of clastic diagenesis. An important contribution of the conceptual models has been to show that clastic sediments undergo considerable change in their mineralogical composition as diagenesis occurs. Mineralogical changes due to diagenesis can be categorized as (1) alteration of original grains, (2) transformation of minerals, (3) formation of authigenic phases, and (4) dissolution of existing minerals. Major factors controlling mineralogical changes include the chemical composition of the pore water, the groundwater flow mechanism which transports mass through a sedimentary basin, temperature of the system and time. However, a major difficulty with the conceptual models is that they are prone to a variety of interpretations. Quantitative techniques are required to systematically evaluate the influence of the various parameters that control the observed mineral assemblages. Research by Helgeson et al. (1969), Hiltabrand et al. (1973), Wigley and Plummer (1976), Weaver and Beck (1977), Hutcheon (1981), Arditto (1983) and Kaiser (1984) has demonstrated the applicability of geochemical and thermodynamic modelling techniques to determine potential mineral assemblages which are in equilibrium with formation water. In most of these examples, emphasis was placed on log-activity diagrams or dissolution reactions. While these studies have over-simplified the phase relationships and physical characteristics of the natural system, their considerable success has demonstrated the value of quantitative methods for delineating the bounds for the behaviour of water-rock interactions under a variety of conditions.

Two important parameters influencing the mineralogical changes in deep sedimentary basins are the quantity of groundwater (and associated dissolved mass) within a rock unit and the rate of flow through the porous media. Thus, the major emphasis of this

thesis is directed towards the development of a computer model that can simulate both mass transport through a clastic sedimentary basin and react the dissolved mass with the porous media. This approach basically requires the development of two models. The first is a groundwater flow model that can simulate the physical mass transport processes of advection and dispersion. Advection transports mass with the flow of groundwater and dispersion acts to spread and mix the dissolved constituents. The second model is a geochemical reaction code that can simulate water-rock interactions under a variety of conditions typical of those occurring in a sedimentary basin. The geochemical code is accompanied by a data base of thermodynamic parameters describing a variety of minerals and aqueous species which typically exist in the diagenetic environment. Because groundwater flow codes typically do not consider reactions, and geochemical codes do not transport mass through a flow regime, it is necessary couple these two models before simulations could begin.

Although there are several existing geochemical codes that can simulate water-rock interactions for a variety of natural conditions, they are typically limited in their application to this research because (1) they have insufficient data for studies at temperatures other than 25°C, and especially to 200°C, (2) data are available for only a limited number of the aqueous species that exist in brines, and (3) part of the theoretical basis for these models is invalid when the fluid salinity exceeds 4,000 mg/L NaCl (ionic strength of 0.1). Hence, the specific goals of this research are to:

1. develop a geochemical reaction code suitable for simulating water-rock interactions that occur in clastic sedimentary basins where temperatures may reach 200°C and the groundwater is typically a brine;
2. construct a data base of thermodynamic parameters, valid for temperatures ranging from 0°C to 200°C, for the authigenic phases and dissolved constituents which characterize the minerals and brines in diagenetic environments;

3. develop a suitable groundwater flow and mass transport code for moving dissolved mass through sediments, and couple this code with the geochemical reaction model;
4. undertake a series of sensitivity analyses to demonstrate the applicability of the code.

Early during the research programme it was recognized that existing groundwater flow and mass transport models, geochemical reaction codes and the thermodynamic data for diagenetic phases and aqueous species were not as advanced as originally anticipated. Hence, the proposed numerical model requires considerable development in all three areas. Because the development of a suitable coupled code and accompanying data base is an enormous undertaking, there were two ways in which this thesis could have progressed. The first was to reduce the scope of the study and address only a specific portion of the required model in detail. The second was to undertake a broadly based study concentrating on the vital concepts necessary to build a framework for future research. The latter method was chosen because detailed work would not be useful if the general concepts could not be implemented. In addition, the broadly based approach should identify those areas for further detailed work that are most important.

Each of the research goals introduced here are addressed in turn. Chapter II examines the limitation of the present geochemical modelling codes and their accompanying data bases for modelling water-rock interactions in large sedimentary basins. This chapter presents a theoretical framework upon which a modified geochemical code and its accompanying data base are developed to allow more accurate simulations of mineral precipitation and dissolution reactions in brines. In Chapter III, the limitations of the thermodynamic parameters for studying ion interaction in brines at temperatures other than 25°C are discussed and a model, which provides both values of the ion interaction parameters at 25°C and interpolations from 0°C to 200°C, is presented. A discussion of the

coupled mass transport and geochemical reaction code, including a brief sensitivity analysis designed to demonstrate the applicability of the code, is presented in Chapter IV.

This thesis represents a first study of the concepts of coupled flow, mass transport and reaction modelling, and its application to clastic sedimentary basins characterized by temperatures to 200°C and salinities to 300,000 mg/L NaCl. Accordingly, Chapter V, the conclusion and summary chapter, includes a discussion of the practical and theoretical limitations of the present code and presents recommendations for future research.

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II. EXTENSION OF GEOCHEMICAL MODELLING TECHNIQUES TO BRINES: COUPLING OF THE PITZER EQUATIONS TO PHREEQE¹

INTRODUCTION

The use of numerical models has greatly enhanced our ability to understand the hydrogeological environment. Groundwater flow and mass transport models permit the study of the sensitivity of various hydrogeological parameters and the testing of hypotheses relating to boundary-value problems. While groundwater flow and mass transport models are invaluable in aiding studies of regional groundwater systems, they do not consider the geochemical reactions that occur between the fluids and rock. It is important to consider geochemical reactions in these systems because of their effect on the hydrogeological properties of the rock and hence, the character of the groundwater flow-system. Reactions which lead to the precipitation of minerals, such as carbonates, silicates or clays, can reduce the porosity and/or permeability of the formation. Reactions that can cause the porous media to dissolve will increase porosity and/or permeability.

This chapter discusses a numerical model developed to study geochemical reactions in the hydrogeological environments of deep sedimentary basins. Sedimentary basins experience a variety of physical and chemical stresses which result in widespread variations in groundwater flow rates, mass transport, temperature, pressure and relative reaction rates among the solid phases and dissolved species. Conventional geochemical modelling techniques are inappropriate for hydrogeological systems in which the chemical character of groundwater is typically a brine and temperatures may reach 200°C because of the thermodynamic theory upon which these models are based. The approach taken here to overcome these obstacles is to modify an existing geochemical code by incorporating proven techniques for electrolyte studies in highly saline solutions, and to modify the

1. A version of this chapter has been published. Crowe, A.S. and F.J. Longstaffe, 1987, in *Proceedings of Solving Ground Water Problems with Models*, National Water Well Association Conference, February 10-12, 1987, Denver, Colorado, pp. 110-129.

model's data base of thermodynamic parameters for the aqueous species and minerals to account for water-rock reactions in these hydrogeological systems.

GEOCHEMICAL BACKGROUND

Basic Thermodynamic Principles

In general, there are two approaches available for modelling geochemical reactions; kinetic and equilibrium. The non-equilibrium or kinetic approach, in which the amount of product increases and the volume of the reactant decreases with time, is the most appropriate for describing the geochemical reactions in a natural system. Unfortunately, most reactions are so poorly characterized that the kinetic approach is not widely practical at this time. In contrast, an equilibrium approach implies that the amount of product and reactant remains constant with time (at a specific temperature and pressure). Equilibrium will be attained only if the groundwater remains in contact with the porous media for a sufficient length of time. The ability of a system to attain equilibrium is directly related to the velocity of the groundwater (Haung et al., 1986). Thus, both the quality of the groundwater and the rate of flow, in addition to the geochemical reaction rate, are very important in controlling mineral stability. If reaction rates are considerably faster than the physical processes affecting mass transport (i.e. the distribution of mass is dominated by geochemical reactions rather than by advection or dispersion), an equilibrium model can be assumed for the system (Palciauskas and Domenico, 1976, Rubin, 1983, Schwartz and Longstaffe, *in press*). Because groundwater flow rates, and hence mass transport in deep sedimentary basins, are very slow, and because the reaction rates for mineral dissolution or precipitation (Langmuir and Mahoney, 1985) are considerably faster than the time scale for these systems to evolve, the equilibrium approach has been successfully applied to rock/brine studies in sedimentary basins by Kramer (1969), Merino (1975), Palciauskas and Domenico (1976), Nesbitt, (1980, 1985), Hutcheon (1981), Land and Prezbindowski

(1981), Walgenwitz et al. (1981) and Kaiser (1984). The equilibrium approach is adopted for this study.

Geochemical reactions within an equilibrium framework are based upon stoichiometric and thermodynamic techniques that maintain balances of mass, charge and energy among all the components within an aqueous system. The mass balance implies that the total mass of an element in the system must always be conserved among all phases, even though the relative proportions of each phase may change. Mathematically this conservation statement can be expressed as:

$$\sum \zeta_{i,(tot)} = \sum \zeta_{i,(aq)} + \sum \zeta_{i,(s)} + \sum \zeta_{i,(g)} \quad (1)$$

where: $\zeta_{i,(tot)}$ = total mass of element i in the system
 $\zeta_{i,(aq)}$ = mass of an aqueous species containing element i
 $\zeta_{i,(s)}$ = mass of a solid phase containing element i
 $\zeta_{i,(g)}$ = mass of element i present as a gas

The charge balance indicates that the total equivalent concentration of all ions with a positive charge are balanced by the equivalent concentration of all ions with a negative charge, including the oxidation-reduction reactions. Typically, the concentration of mass in solution is measured with units of molality (m). An equivalent concentration is the molality of a species multiplied by its charge. The mathematical expression for the mass balance is:

$$\sum m_c \cdot z_c \text{ (cations)} + \sum m_a \cdot z_a \text{ (anions)} = 0 \quad (2)$$

where: m_c = molality of a cation in the solution
 z_c = charge of the cation
 m_a = molality of an anion
 z_a = charge of an anion
 $m \cdot z$ = equivalent concentration

The energy balance is based on the available energy or Gibbs free energy of each component in the system. In an ideal system, the free energy will vary linearly with the log of the molality of the component. However, real systems do not exhibit ideal behaviour and deviations from ideality occur. Thus, in non-ideal systems, it is necessary to replace molal concentrations by thermodynamically effective concentrations or activities (a). For every component, a standard state or reference state can be defined at specified conditions of temperature, pressure and chemical composition, and at the reference state a value of Gibbs free energy is defined. The free energy of components in real systems are referenced to its value at standard state. The Gibbs free energy of a component in a real system is expressed as:

$$G_i = G_i^\circ + RT \ln a_i \quad (3)$$

where: G_i = Gibbs free energy of component i
 G_i° = Gibbs free energy of component i at standard state
 R = gas constant
 T = temperature
 a_i = activity of component i

At equilibrium, the free energy of formation of a component from its elements will balance. Therefore, by definition:

$$G_{f,i} = \sum_j^n G_j \text{ (products)} + \sum_k^m G_k \text{ (reactants)} = 0 \quad (4)$$

where: $G_{f,i}$ = Gibbs free energy of formation of component i
 G_j = Gibbs free energy of the n product components
 G_k = Gibbs free energy of the m reactant components

Substituting equation (4) into equation (3) simplifies the expression of the Gibbs free energy of a component in a real system to:

$$-G_{f,i}^{\circ} = RT \ln a_i \quad (5)$$

where: $G_{f,i}^{\circ}$ = Gibbs free energy of formation of component i at standard state

The free energy of a reaction can be expressed by summing the free energies of formation of the standard state values of the products and the reactants according to the following equations:

$$\Delta G_R^{\circ} = \sum_j^n G_{f,j}^{\circ} \text{ (products)} - \sum_k^m G_{f,k}^{\circ} \text{ (reactants)} \quad (6)$$

where: G_R° = Gibbs free energy of the reaction at standard state
 $G_{f,j}^{\circ}$ = Gibbs free energy of the n products at standard state
 $G_{f,k}^{\circ}$ = Gibbs free energy of the m reactants at standard state

Substituting equation (4) into equation (5) gives an equilibrium expression relating the activity of the components to the free energy of the reaction:

$$-\Delta G_R^{\circ} = RT \sum_i^n \ln a_i \quad (7)$$

where: a_i = activity of the components of the reaction

From equation (7) it can be seen that the activities of the products and the reactants are expressed as a ratio. When the reaction is at equilibrium, this ratio is a constant, and the equation describing this relationship is known as the *Law of Mass Action*. For example, a general reaction at equilibrium between reactants B and C and products X, Y and Z can be written as:



where: B, C = reactant components

X, Y, Z = product components

b, c = stoichiometric constants of the reactant components

x, y, z = stoichiometric constants of the product components

The *Law of Mass Action* can be written for this reaction and the ratio of the activities is known as the equilibrium constant:

$$K_{eq} = \frac{a_X^x \cdot a_Y^y \cdot a_Z^z}{a_B^b \cdot a_C^c} \quad (9)$$

where: K_{eq} = the equilibrium constant

a_X^x, a_Y^y, a_Z^z = activity of the reactant components X, Y, Z

a_B^b, a_C^c = activity of the product components B, C

A standard state is typically defined for solids such that the activity of a pure solid, in its stable form, is equal to 1. The activity of a gas that is in equilibrium with a solution is usually assumed to be equal to the partial pressure of the gas.

Equation (9) can be substituted into equation (7) yielding an expression relating the standard state Gibbs free energy of a reaction to the equilibrium constant:

$$-\Delta G_R^\circ = RT \ln K_{eq} \quad (10)$$

Values of the equilibrium constant are generally calculated using equation (10). Because K_{eq} is a constant at equilibrium, a change in the activity of one component within the reaction must result in a change in the activity of other components if the value of K_{eq} is to remain constant, and hence equilibrium is to be maintained.

The activity coefficient is a measure of the deviation of a solution from ideality. It relates the laboratory measurement of concentration, molality, to activity by the following expression:

$$a_i = \gamma_i m_i \quad (11)$$

where: γ_i = activity coefficient of component i
 m_i = molality of component i

The activity coefficient of an aqueous species is strongly dependent upon the salinity of the solution. In infinitely dilute solutions, the activity coefficient is unity and the molality of a species equals the activity of the species. As the salinity of the solution increases, the activity coefficient becomes increasingly less than one. The thermodynamic term analogous to salinity is ionic strength. The ionic strength is a measure of the electrical attractions and repulsions among all ions within a solution. It is defined by:

$$I = \frac{1}{2} \sum_i m_i \cdot z_i^2 \quad (12)$$

where: I = ionic strength
 m_i = molality of ion i
 z_i = charge of ion i

The technique used to determine the activity coefficient is of particular concern because it strongly influences the calculations which determine the distribution of mass as either minerals or aqueous species. Activity coefficients of ions cannot be measured directly; they can only be obtained using theoretical models (Stumm and Morgan, 1981). Several models have been developed to predict the activity coefficients of ions in electrolyte solutions. Most equations are based upon the Debye-Hückel theory, in which activity coefficients are calculated on the basis of the effects of temperature, pressure, charge of the ion, ionic strength of the solution and electrostatic effects of water. These models will be referred to as single ion models because the calculated activity coefficient is for a single ion in solution.

The Debye-Hückel equation is normally used to calculate the activity coefficients of ions in waters of low salinity, and is valid to an ionic strength of approximately 0.1 (approximately 6000 mg/L NaCl). This activity coefficient model accounts for the hydrated radius of the ion, as well as the electrostatic effects of water, and is written as:

$$\log \gamma_i = -|z_i|^2 \frac{A\sqrt{I}}{1 + Ba_0\sqrt{I}} \quad (13)$$

where: A = the Debye-Hückel limiting slope, which is a solvent parameter dependent upon properties of the solution
 B = another solvent parameter, and is a function of properties of the solution
 a₀ = adjustable parameter related to the hydrated radius of the ion

As the solution becomes more saline, the activity coefficient becomes increasingly influenced by the interaction among ions in the solution. To extend the accuracy of the Debye-Hückel equation to an ionic strength of 0.5, an additional empirical term, specific to each particular ion, is added, giving the extended Debye-Hückel equation:

$$\log \gamma_i = -|z_i|^2 \frac{A\sqrt{I}}{1 + Ba_0\sqrt{I}} + b_i I \quad (14)$$

where b_i = an adjustable parameter corresponding to a specific ion, and accounts for changes to the ion in very saline solutions

A generalized form of the extended Debye-Hückel equation was proposed for ions that do not have ion parameters that are required by the Debye-Hückel equations. It is also more applicable than the Debye-Hückel equations for solutions containing several electrolytes. This equation, valid to an ionic strength of approximately 0.5, is known as the Davies equation:

$$\log \gamma_i = -|z_i^2| A \left(\frac{\sqrt{I}}{1 + \sqrt{I}} + CI \right) \quad (15)$$

where: C = an empirical parameter set to 0.2 or 0.3 (Stumm and Morgan, 1981)

Formulae for calculating the Debye-Hückel solvent parameters A and B are given by Stumm and Morgan (1981) and Truesdell and Jones (1974), while values at specific temperatures are compiled by Nordstrom and Munoz (1985). The ion size parameters a_0 and b_i are tabulated in Truesdell and Jones (1974), Stumm and Morgan (1981) and Nordstrom and Munoz (1985).

The activity coefficients of the Na^+ , Cl^- , Ca^{+2} and SO_4^{2-} ions are calculated by the three single ion models (equations (13), (14) and (15)) to illustrate the behaviour of the three models as a function of the ionic strength of a solution. For these calculations, the solution is based upon the chemical character of the composition of sea water (Stumm and Morgan, 1981) at an ionic strength of 0.72. In order to vary the ionic strength of the solution, the species is either concentrated or diluted by the removal or addition of pure water and without the precipitation of salts. Hence, while the concentration of each species changes, their relative proportions remain constant.

The activity coefficients calculated by these three equations diverge as the salinity of the solution increases (Figure 1). This occurs because some of the assumptions upon which the Debye-Hückel theory is derived become invalid at high ionic strengths. These assumptions include (1) the hydrated radius of the ion does not change with varying ionic strengths, (2) the electrostatic effects remain linear as salinity increases to high concentrations, (3) ions within the solution do not interact, and (4) the activity coefficient is independent of the chemical composition of the solution.

Several numerical models which can be used to describe the dissolution and precipitation of minerals and the distribution of dissolved mass among various species

within aqueous systems in geological settings currently exist. Examples of these geochemical codes include *SOLMNEQ* (Kharaka and Barnes, 1973), *WATEQF* (Plummer et al., 1976), *MINEQL* (Westall et al., 1976), *EQ3/EQ6* (Wolery, 1979) and *PHREEQE* (Parkhurst et al., 1980). All of these numerical models describe geochemical reactions within an equilibrium framework, and are based upon the above thermodynamic and stoichiometric theory. The models can be applied to a variety of geochemical studies involving aqueous systems. An example showing the the solubility of gypsum in a NaCl solution, with an ionic strength varying from 0.0 to 5.0, as calculated by the geochemical codes *SOLMNEQ*, *PHREEQE* and *WATEQF* is illustrated with Figure 2. Because equations (13), (14) and (15) are commonly incorporated into these geochemical codes to serve as the technique for calculating the activity coefficient, these models can be successfully applied to aqueous systems only at low salinities. At ionic strengths typically above 1.0, the calculated solubility is dramatically larger than that determined experimentally. Thus, a different technique is required for accurately predicting mineral solubility in highly saline solutions or brines.

The Pitzer Equations

The recent technique developed by Pitzer and his co-workers has extended our ability to predict values of the activity coefficient of electrolytes or ions in solutions with a very high ionic strength (Pitzer, 1973, 1975; Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974; Silvester and Pitzer, 1977, 1978). This technique is a specific ion interaction model, and thus accounts for the effects of ion interactions that occur at a high ionic strength. The specific ion interaction approach calculates a stoichiometric activity coefficient based upon the total concentration of all the chemical components in the solution. In contrast, single ion models are used to calculate of an activity coefficient for a distinct species based on the ionic strength of the solution. Other specific ion interaction models which may be used to calculate activity coefficients in highly saline solutions include the

Guggenheim equations (Guggenheim and Turgeon, 1955), the Harned equations (Harned and Owen, 1958) and the Scatchard equations (Scatchard, 1961; Scatchard, 1968). We have chosen the Pitzer equation model for our study because (1) it accurately reproduces experimental data in solutions ranging from dilute to highly concentrated brines; (2) the technique is widely used in electrolyte chemistry; (3) these equations require relatively few parameters; (4) data are available for a multitude of electrolyte solutions; and (5) this model has been successfully applied to a variety of geological studies (Whitfield, 1975a, 1975b; Harvie and Weare, 1980; Harvie et al., 1982, 1984; Gueddari et al., 1983; Monnin and Schott, 1984, Brantley et al., 1984).

The Pitzer equation model for activity coefficients combines the Debye-Hückel term for the electrostatic theory of ions in solution with a virial series for the short range forces among ions, and is based on the differentiation of the equation for excess Gibbs free energy. The virial expansion expresses the activity coefficient as a power series written as a function of ionic strength. The virial coefficients comprising the equation are empirical terms determined through a regression analysis of experimental data to high ionic strengths. Pitzer (1973) starts with a virial expansion of the excess Gibbs free energy because the activity coefficient can be derived from this expression. The excess Gibbs free energy is defined as:

$$G^{ex} = G^{ideal} - G^{real} \quad (16)$$

where: G^{ex} = excess Gibbs free energy
 G^{ideal} = Gibbs free energy of an ideal system
 G^{real} = Gibbs free energy of a real system

Substituting equation (11) into equation (5) gives an expansion of the Gibbs free energy of a real species in terms of its molality and activity coefficient:

$$-G^{real} = RT \ln m_i + RT \ln \gamma_i \quad (17)$$

Because the activity of a species equals its molality in an ideal system (i.e. $\gamma = 1$), the ideal Gibbs free energy can be defined as:

$$G^{\text{ideal}} = -RT \ln m_i \quad (18)$$

Substituting equations (17) and (18) into equation (16) gives:

$$G^{\text{ex}} = RT \ln \gamma_i \quad (19)$$

The virial expansion of this expression of excess Gibbs free energy in terms of molality is given by Pitzer (1973) as:

$$\frac{G^{\text{ex}}}{RT} = n_w [f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k] \quad (20)$$

- where: n_w = number of kilograms of solvent
 $f(I)$ = term related to the ionic strength of the solution and accounts for long range electrostatic effects (the Debye-Hückel term)
 $\lambda_{ij}(I)$ = term to account for short range interaction between ion pairs
 μ_{ijk} = term to account for triple ion interaction at high ionic strengths

Taking the derivative of this expression and combining terms relating to single, double and triple ion interactions yields the following expressions for the activity coefficients of electrolytes, cations, anions and neutral species:

$$\begin{aligned} \ln \gamma_{MX} = & |z_M z_X| f(I) + \left(\frac{2v_M}{v} \right) \sum_a m_a [B_{Ma} + EC_{Ma} + \frac{v_X}{v_M} \Theta_{Xa}] + \\ & \left(\frac{2v_X}{v} \right) \sum_c m_c [B_{cX} + EC_{cX} + \frac{v_M}{v_X} \Theta_{Mc}] + \\ & \sum_c \sum_a m_c m_a \{ |z_M z_X| B'_{ca} + \frac{1}{v} (2v_M z_M C_{ca} + v_M \psi_{Mca} + v_X \psi_{caX}) \} + \\ & \frac{1}{2} \sum_c \sum_c m_c m_c \left(\frac{v_X}{v} \psi_{ccX} + |z_M z_X| \Theta'_{cc} \right) + \frac{1}{2} \sum_a \sum_a m_a m_a \left(\frac{v_M}{v} \psi_{Maa} + |z_M z_X| \Theta'_{aa} \right) + \\ & \sum_a m_a \lambda_{aM} + \sum_a m_a \lambda_{aX} \end{aligned} \quad (21)$$

$$\ln \gamma_M = z_M^2 f'(I) + \sum_a m_a [2B_{Ma} + EC_{Ma}] + 2 \sum_c m_c \Theta_{Mc} + \sum_c \sum_a (\psi_{Mca} + |z_M| C_{ca}) + \sum_a \sum_a m_a m_a (\psi_{Maa}) + 2 \sum_n m_n \lambda_{nM} \quad (22)$$

$$\ln \gamma_X = z_X^2 f'(I) + \sum_c m_c [2B_{cX} + EC_{cX}] + 2 \sum_a m_a \Theta_{Xa} + \sum_c \sum_a (\psi_{caX} + |z_X| C_{ca}) + \sum_c \sum_c m_c m_c (\psi_{ccX}) + 2 \sum_n m_n \lambda_{nX} \quad (23)$$

$$\ln \gamma_N = \sum_c m_c (2\lambda_{Nc}) + \sum_a m_a (2\lambda_{Na}) + \sum_n m_n (2\lambda_{Nn}) \quad (24)$$

- where:
- γ_{MX} = activity coefficient of an electrolyte
 - γ_M = activity coefficient of a cation
 - γ_X = activity coefficient of an anion
 - γ_N = activity coefficient of a neutral species
 - M = subscript for the cation of interest
 - X = subscript for the anion of interest
 - N = subscript for the neutral species of interest
 - z = charge of the ions
 - $f'(I)$ = Debye-Hückel term (defined below)
 - m = molality of the ion or neutral species in solution
 - c = subscript for the cations in solution
 - a = subscript for the anions in solution
 - n = subscript for the neutral species in solution
 - B = second virial coefficient for cation-anion interactions
 - B' = second virial coefficient for cation-anion interactions
 - C = third virial coefficient for cation-anion interactions
 - E = an equivalent concentration (defined below)
 - Θ = second virial coefficient accounting for short-range interaction between ion pairs of like signs in electrolyte mixtures
 - Θ' = second virial coefficient accounting for short-range interaction between ion pairs of like signs in electrolyte mixtures
 - λ = second virial coefficient accounting for interaction between neutral species and ions
 - ψ = third virial coefficient accounting for triple ion interactions in electrolyte mixtures, calculated from a least squares fit

- ν_M = number of cations in the chemical formula of the ion pair
 ν_X = number of anions in the chemical formula of the ion pair
 ν_A = total number of ions in the chemical formula ($\nu_M + \nu_X$)

The electrostatic term considering the Debye-Hückel effects is a function of the ionic strength of the solution and is defined as:

$$f^E(I) = -A^* \left(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{5} \ln[1 + b\sqrt{I}] \right) \quad (25)$$

- where: A^* = Debye-Hückel constant for the osmotic coefficient (Bradley and Pitzer, 1979)
 b = empirical constant set to 1.2 (Pitzer, 1973)

The terms accounting for cation-anion interactions are the second virial coefficients, defined as a function of regression parameters:

$$B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} g(x_1) + \beta_{ca}^{(2)} g(x_2) \quad (26)$$

$$B'_{ca} = \beta_{ca}^{(1)} \left(\frac{g'(x_1)}{I} \right) + \beta_{ca}^{(2)} \left(\frac{g'(x_2)}{I} \right) \quad (27)$$

- where: $\beta_{ca}^{(0)}, \beta_{ca}^{(1)}$ = regression parameters for 1:1, 2:1 or 1:2 electrolytes
 $\beta_{ca}^{(2)}$ = regression parameters for 2:2 electrolytes
 $g(x), g'(x)$ = empirical functions based upon the ionic strength of the solution

The values of $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$ and $\beta_{ca}^{(2)}$ are determined for each electrolyte pair by a least squares fit of experimentally determined values of activity or osmotic coefficients. The functions $g(x)$, $g'(x)$ and the terms x_1 and x_2 are expressed as:

$$g(x) = \frac{2(1 - (1+x)e^{-x})}{x^2} \quad (28)$$

$$g'(x) = \frac{2(-1 + (1+x + \frac{x^2}{2})e^{-x})}{x^2} \quad (29)$$

$$\text{where: } x_1 = \alpha_1 \sqrt{I} \quad \text{for all electrolytes} \quad (30)$$

$$x_2 = \alpha_2 \sqrt{I} \quad \text{for 2:2 or higher electrolytes} \quad (31)$$

The values of α_1 and α_2 are empirical terms defined by:

$\alpha_1 = 2.0$	for 1:1, 1:2, 2:1, 1:3 and 3:1 electrolytes (Pitzer, 1973)
$\alpha_1 = 1.4$	for 2:2 electrolytes (Pitzer and Mayorga, 1979)
$\alpha_1 = 2.0$	for 3:2 or 2:3 and higher electrolytes (Pitzer and Silvester, 1978)
$\alpha_2 = 12.0$	for 2:2 electrolytes (Pitzer and Mayorga, 1979)
$\alpha_2 = 50.0$	for 2:3, 3:2 and higher electrolytes (Pitzer and Silvester, 1978)

The Pitzer equations require a third virial coefficient to account for cation-anion interactions that occur in solutions characterized by very high salinities. The term has the form:

$$C_{ca} = \frac{C_{ca}^{\dagger}}{2\sqrt{z_c z_a}} \quad (32)$$

where: $C_{ca}^{\dagger}$ = regression parameter chosen for each electrolyte by a least squares fit of experimental data

The equivalent concentration term (E) is defined by:

$$E = \sum_i m_i |z_i| \quad (33)$$

Terms accounting for short range cation-cation and anion-anion interactions in solutions of mixed electrolytes are also needed for mixed electrolyte solutions. These terms are included

by Pitzer and Kim (1974) to account for the influence that ions of the same sign (either +ve or -ve) have on the second and third virial coefficient and are expressed as:

$$\Theta_{ij} = \theta_{ij} + {}^E\Theta_{ij}(I) \quad (34)$$

$$\Theta'_{ij} = {}^E\Theta'_{ij}(I) \quad (35)$$

where: θ_{ij} = term for the short-range interaction between ions calculated from a least squares fit

${}^E\Theta_{ij}(I)$ = term for electrostatic interaction between ions of like charge, based on ionic strength

${}^E\Theta'_{ij}(I)$ = term for electrostatic interaction between ions of like charge, based on ionic strength

The ionic strength dependent terms (${}^E\Theta_{ij}(I)$ and ${}^E\Theta'_{ij}(I)$) are evaluated with the following functions:

$${}^E\Theta_{ij}(I) = \frac{Z_i Z_j}{4I} \left(J(x_{ij}) - \frac{1}{2}J(x_{ii}) - \frac{1}{2}J(x_{jj}) \right) \quad (36)$$

$${}^E\Theta'_{ij}(I) = \frac{{}^E\Theta_{ij}(I)}{I} + \frac{Z_i Z_j}{8I^2} \left(x_{ij}J'(x_{ij}) - \frac{1}{2}x_{ii}J'(x_{ii}) - \frac{1}{2}x_{jj}J'(x_{jj}) \right) \quad (37)$$

$$x_{ij} = 6Z_i Z_j A^* \sqrt{I} \quad (38)$$

$$J(x_{ij}) = \frac{1}{4}x - 1 + \frac{1}{x} \int_0^{\infty} (1 - e^{-x/y} e^{-y}) y^2 dy \quad (39)$$

$$J'(x_{ij}) = \frac{1}{4} - \frac{1}{x^2} \int_0^{\infty} \left(1 - \left(1 + \frac{x}{y} e^{-y} \right) e^{-x/y} e^{-y} \right) y^2 dy \quad (40)$$

The values of ${}^E\Theta_{ij}(I)$ and ${}^E\Theta'_{ij}(I)$ are 0 when the charges of the two ions are equal.

Figure 3 illustrates the accuracy of the specific ion interaction model of Pitzer for reproducing experimental values of the mean activity coefficients of electrolytes to very high salinities. In this example, the solvent is pure water. Activity coefficients of single ions are not measurable and hence can only be determined through theoretical expressions. However, the mean activity coefficient of electrolyte solutions can be derived by well known experimental techniques (Stumm and Morgan, 1981). Also shown by these four diagrams are the mean activity coefficients calculated by the single ion models (equations (13), (14) and (15)). Activity coefficients can be calculated accurately by all models within the dilute range where ion interaction is negligible, but only the Pitzer equations consistently reproduce mean activity coefficients over the entire range of salinities. Because only the Pitzer equations account for ion interactions, the single ion model and the specific ion interaction model are not exactly equivalent in very saline solutions and the results are, as expected, different. A more realistic comparison would be to use a single ion model and consider all the ion pairs that occur at high ionic strengths. However, as will be discussed in more detail below, the shape of the curves for the single ion models will not change significantly. The actual proof of the validity of the Pitzer equations versus the single ion model will become evident later when the mineral solubility calculations are presented. But for the purpose of illustrating the models for calculating activity coefficients that are presently incorporated into geochemical codes, and the differences among the calculated activity coefficients, results from both models are presented here.

This next set of simulations examines the activity coefficients calculated for ions in solutions of varying chemical composition. The chemical constituents used in this example are initially based on a sea water composition given by Whitfield (1975a). However, in order to produce hypothetical aqueous systems each with specific chemical characteristics, the concentrations of the ions have been adjusted so that the solution has one dominant cation or one dominant anion accounting for 95% of the equivalent concentration. A value of 95% was arbitrarily chosen to represent extreme geochemical cases for the purpose of

illustrating the behaviour of calculated values of the activity coefficient. The remaining cations and anions comprise 5% of the mass. The initial sea water composition and the chemical character of the solutions after the transformation of sea water to solutions dominated by one cation-anion pair are listed in Table 2.1. The change in composition was made by maintaining a constant equivalent concentration. The salinity is then increased or decreased by either the removal or addition of water, respectively, without the precipitation of salts. Figure 4a shows the activity coefficients of the cation (Na^+) which is the dominant cation in the solution. Figure 4b is a similar analysis but with a dominant anion (Cl^-) and different major cations. Figure 4c is an analysis of a cation (Ca^{+2}) which is not the dominant cation in any of these three solutions. Figure 4d illustrates the behaviour of the activity coefficients of a cation (Mg^{+2}) which comprises 95% of the cations in the Mg-Cl solution and is a minor species in the Na-Cl and Na- CO_3 solutions. Activity coefficients are calculated with three single ion models and with the Pitzer equations.

Results of these simulations are illustrated by Figure 4. The aqueous species are grouped into four categories defined using the following terminology:

free ions:

mono-atomic ions or strongly bonded complexes, such as Na^+ , Ca^{+2} , Cl^- , OH^- and SO_4^{2-} ;

ion pairs:

species representing the interaction of a cation and an anion which are treated as a single chemical entity, for example CaCl^+ , NaCl^0 , $\text{Ca}(\text{OH})_2^0$ and NaSO_4^- ;

neutral species:

a subset of the ion pairs consisting of species with a charge of zero, such as CaCl_2^0 , NaCl^0 and Na_2SO_4^0 ;

stoichiometric component:

a group of species with a common cation or anion, where the stoichiometric component Na refers to $\text{Na}^+ + \text{NaCl}^0 + \text{NaSO}_4^- + \text{Na}_2\text{CO}_3^0 + \dots$

An activity coefficient calculated using these single ion models is essentially independent of the chemical character of the solution because, as is evident in equations (13) and (15),

Table 2.1: The chemistry of sea water and the solutions with a dominant cation and anion.

cations	sea water ¹ (molality)	sea water (epm) ²	95% Na ⁺ (molality)	95% Ca ⁺² (molality)	95% Mg ⁺² (molality)
Na ⁺	0.470x10 ⁰	0.470x10 ⁰	0.578x10 ⁰	0.243x10 ⁻¹	0.285x10 ⁻¹
K ⁺	0.101x10 ⁻¹	0.101x10 ⁻¹	0.222x10 ⁻²	0.523x10 ⁻³	0.613x10 ⁻³
Ca ⁺²	0.104x10 ⁻¹	0.208x10 ⁻¹	0.229x10 ⁻²	0.289x10 ⁰	0.631x10 ⁻³
Mg ⁺²	0.536x10 ⁻¹	0.107x10 ⁰	0.118x10 ⁻¹	0.277x10 ⁻²	0.289x10 ⁰
Mn ⁺²	0.360x10 ⁻⁷	0.720x10 ⁻⁷	0.792x10 ⁻⁸	0.186x10 ⁻⁸	0.219x10 ⁻⁸
Fe ⁺²	0.540x10 ⁻⁷	0.108x10 ⁻⁶	0.119x10 ⁻⁷	0.280x10 ⁻⁸	0.328x10 ⁻⁸
Sr ⁺²	0.970x10 ⁻⁴	0.194x10 ⁻³	0.213x10 ⁻⁴	0.502x10 ⁻⁵	0.589x10 ⁻⁵
Ba ⁺²	0.220x10 ⁻⁶	0.440x10 ⁻⁶	0.484x10 ⁻⁷	0.114x10 ⁻⁷	0.134x10 ⁻⁷
Ni ⁺²	0.340x10 ⁻⁷	0.680x10 ⁻⁷	0.748x10 ⁻⁸	0.176x10 ⁻⁸	0.206x10 ⁻⁸
Co ⁺²	0.130x10 ⁻⁸	0.260x10 ⁻⁸	0.286x10 ⁻⁹	0.673x10 ⁻¹⁰	0.789x10 ⁻¹⁰
Cu ⁺²	0.100x10 ⁻⁶	0.200x10 ⁻⁶	0.220x10 ⁻⁷	0.518x10 ⁻⁸	0.607x10 ⁻⁸
Zn ⁺²	0.760x10 ⁻⁷	0.152x10 ⁻⁶	0.167x10 ⁻⁷	0.393x10 ⁻⁸	0.461x10 ⁻⁸

anions	sea water ¹ (molality)	sea water (epm) ²	95% Cl ⁻ (molality)	95% SO ₄ ⁻² (molality)	95% CO ₃ ⁻² (molality)
Cl ⁻	0.552x10 ⁰	0.552x10 ⁰	0.579x10 ⁰	0.304x10 ⁻¹	0.304x10 ⁻¹
SO ₄ ⁻²	0.281x10 ⁻¹	0.562x10 ⁻¹	0.297x10 ⁻¹	0.579x10 ⁰	0.281x10 ⁻²
CO ₃ ⁻²	0.300x10 ⁻³	0.600x10 ⁻³	0.317x10 ⁻³	0.331x10 ⁻⁴	0.579x10 ⁰
Br ⁻	0.850x10 ⁻³	0.850x10 ⁻³	0.449x10 ⁻³	0.468x10 ⁻⁴	0.425x10 ⁻⁴
F ⁻	0.740x10 ⁻⁴	0.740x10 ⁻⁴	0.391x10 ⁻⁴	0.408x10 ⁻⁵	0.370x10 ⁻⁵
I ⁻	0.470x10 ⁻⁶	0.470x10 ⁻⁶	0.248x10 ⁻⁶	0.259x10 ⁻⁷	0.235x10 ⁻⁷

1: values from Whitfield (1975a).

2: sea water as an equivalent concentration.

these equations consider only the ionic strength of the solution and not the molality of the ion of interest. For example, the activity coefficients of Mg^{+2} in a 95% Na-Cl solution, where Mg^{+2} is a minor species, is the same as the activity coefficient of Mg^{+2} in a 95% Mg-Cl solution, where Mg^{+2} is the dominant cation (Figure 4d). In contrast, the Pitzer equations (equations (21) to (24)), are a function of both the ionic strength of the solution and its chemical characteristics. Hence, these activity coefficients are different for each solution (Figure 4). If the activity coefficients of the free ions were recalculated with the Debye-Hückel or Davies equations after accounting for ion pairing, the shape of the curves within Figure 4 would not change significantly. The effect of ion pairing is to redistribute mass from free ions to ion pairs which have a lower absolute charge than the free ion (e.g. Ca^{+2} to $CaCl$, $CaCl_2^0$, $CaOH^+$, $Ca(OH)_2^0$, etc.). Thus, because the charge of the ion pairs are smaller, the ionic strength calculated by equation (12) decreases even though the total mass of a component remains constant. Thus, accounting for ion pairs with a single ion model results in a change in the value of the activity coefficient of the free ion along its activity coefficient versus ionic strength curve (Figure 4) as the ionic strength of the solution decreases. However, because the mass has been redistributed from free ions to ion pairs, the solubility of minerals, as calculated by equation (9), changes. This behaviour is discussed in more detail within the next section.

AN IMPROVED GEOCHEMICAL CODE

The previous section illustrates the importance of using an accurate technique for calculating activity coefficients in very saline solutions or brines. The development of a geochemical model utilizing the Pitzer equations and the data base for this model are discussed in this section. While there have been successful applications of the Pitzer equations to mineral solubility studies (Whitfield, 1975a, 1975b, Harvie and Weare, 1980, Harvie et al., 1982, 1984, Gueddari et al., 1983, Monnin and Schott, 1984), these studies have not utilized a general geochemical reaction code. There is current interest in modifying

some of the existing codes, such as *SOLMNEQ*, *EQ3/6* or *MINEQL*, to include the Pitzer equations there are no recent publications that would indicate that this work has been done. To date, the present codes are still being constructed or in a verification stage of development (Pabalan, Kharaka, *pers. comm.*). The application of the model to studies of mineral stability in brines is presented to illustrate the need for specific ion interaction techniques as part of geochemical codes that deal with highly saline fluids.

Rather than develop another numerical model, an existing computer code, known as *PHREEQE* (Parkhurst et al., 1980) was modified for this study. *PHREEQE* was chosen because (1) the model is well documented and has several example problems included in the user's manual, (2) the computer code is also well documented with comment cards which makes modifications to the code relatively easy, and (3) *PHREEQE* has been extensively and successfully validated through application to a variety of problems.

The theoretical framework, operation and application of *PHREEQE* is described in detail by Parkhurst et al. (1980), Plummer et al. (1983) and Plummer (1985). For a thorough description of the code, the reader is referred to these publications; only a brief discussion is presented here. *PHREEQE* is a geochemical modelling code designed to describe speciation, mineral solubility, redox conditions and mass transfer under equilibrium conditions. The user defines the initial conditions of the system by specifying pH, pe, solution chemistry, minerals present and temperature. The program adjusts these parameters to ensure that the starting solution is chemically balanced. Next, mass is transferred among the aqueous species and solid phases by using the balance equations for mass and charge and the *Law of Mass Action*, always maintaining equilibrium among the phases.

PHREEQE was modified and updated producing four improved versions of *PHREEQE*. Initial changes to the code include modifying the program so that it can be compiled with VS FORTRAN, modifying the code to decrease its execution time, increasing the limits of the data bases and enhancing the printed output. However, these

initial changes do not include incorporation of the Pitzer equations into the improved code. This new version of *PHREEQE* is designed to run on a mainframe computer and is referred to as *PHREEQEX*.

In addition to the changes made to the code, the data base of species, minerals and gases for *PHREEQE* was expanded for use with *PHREEQEX*. The major parameters in this data base (specified in Appendix 2) consists of a value of (1) $\log K_{eq}$ for the reaction describing the formation of a species from aqueous components and $\log K_{eq}$ for the reaction defining the dissociation of a mineral or a gas into species, (2) an enthalpy value or interpolation function to obtain a value of $\log K_{eq}$ at temperatures other than 25°C, (3) the association or dissociation reaction corresponding to $\log K_{eq}$, and (4) charge related terms. The data base of thermodynamic properties for the species was expanded and now includes approximately 250 species (the majority are ion pairs) formed from the geologically important elements: H, K, Na, Li, Rb, Be, Mg, Ca, Sr, Ba, Ra, Al, Mn, Fe, B, O, Cl, S, C, Si, N, I, F, Br. All the species included within the *PHREEQEX* data base and the corresponding values of $\log K_{eq}$, as well as the source of these data, are listed in Appendix 2 (Table A.10). The selection of minerals in the data base is modified to include approximately 40 chloride, carbonate, sulphate, sulphide, silicate and hydroxide minerals that occur in clastic sedimentary rocks. Also included are the thermodynamic parameters for the gases CO_2 , H_2S , CH_4 , SO_2 , O_2 and H_2 . All the minerals included within the *PHREEQEX* data base, the dissociation reactions, and the corresponding values of $\log K_{eq}$, as well as the source of these data, are also listed in Appendix 2 (Table A.12).

The final modification to the data base deals with obtaining values of the equilibrium constant for the dissociation reaction of minerals and association reactions for the species for temperatures up to 200°C. There are two methods for obtaining these high temperature data. The first method consist of an interpolation function and associated interpolation coefficients that express $\log K_{eq}$ as a function of temperature. To obtain the interpolation function, values of $\log K_{eq}$ must be available for temperatures up to 200°C and

these data are then regressed to derive the interpolation coefficients. The interpolation function used here is the same as that proposed by Parkhurst et al. (1980):

$$\log K_{eq}(T) = a_1 + a_2 \cdot T + a_3 \cdot T^{-1} + a_4 \cdot T^2 + a_5 \cdot T^{-2} \quad (41)$$

where: $\log K_{eq}(T)$ = value of $\log K_{eq}$ at the temperature of interest
 T = temperature of interest
 a_i = interpolation coefficients

Secondly, if an interpolation function is not available, or if the values of $\log K_{eq}$ are known only at temperatures not far from 25°C, the high temperature values of $\log K_{eq}$ are determined with a van't Hoff expression (Parkhurst et al., 1980, Stumm and Morgan, 1981). The van't Hoff expression is defined as:

$$\log K_{eq}(T) = \log K_{eq}(T_R) - \frac{\Delta H_R^\circ}{2.3 \cdot R} \left(\frac{1}{T} - \frac{1}{T_R} \right) \quad (42)$$

where: $\log K_{eq}(T_R)$ = value of $\log K_{eq}$ at the reference temperature
 T_R = reference temperature (298.15K)
 ΔH_R° = enthalpy of the reaction at 25°C

Where possible, an interpolation function is used to obtain the high temperature values for $\log K_{eq}$ because these functions are more accurate at high temperatures than extrapolations made with the van't Hoff expression. Interpolation functions are provided for all the minerals in the *PHREEQEX* data base, but are available for only a few of the species. Values of the coefficients for the equations used to interpolate the values of the equilibrium constants for the mineral are contained in Table A.13 of Appendix 2. Values of enthalpy for the association reaction (ΔH_R°) at 25°C for the species are required by the van't Hoff expression. These data, as well as the interpolation coefficients for the high

temperature interpolation functions for the species are listed in Tables A.10 and A.11 of Appendix 2, respectively.

The values of $\log K_{eq}$, ΔH_R° and the data used to determine the interpolation coefficients for calculating $\log K_{eq}$ at high temperatures are obtained from a number of sources. The data are selected, in order of preference, from the following sources:

- (1) U.S. National Bureau of Standards Technical Notes (Wagman et al., 1968, 1969, 1971, 1981 and 1982, Parker et al., 1971, Schumm et al., 1973);
- (2) Baes and Mesmer (1976);
- (3) the original *PHREEQE* data base (Parkhurst et al., 1980);
- (4) the *WATEQ* or *WATEQF* data bases (Truesdell and Jones, 1973, Plummer et al., 1976);
- (5) the *SOLMNEQ* data base (Kharaka and Jones, 1974).

The U.S. National Bureau of Standards Technical Notes contains a very large compilation of thermodynamic properties of species which have been evaluated for accuracy and consistency. Thus, these publications are the primary source of data for the *PHREEQEX* data base. Values of ΔG_f° and ΔH_f° of the species comprising the association reactions are obtained from this source, and used to calculate ΔG_R° and ΔH_R° at 25°C, respectively, with equation (6). The value of $\log K_{eq}$ is calculated with ΔG_R° by equation (10). Also, values of entropy (S°) and heat capacity (C_p°) obtained from these publications are used to calculate $\log K_{eq}$ at high temperatures. These values are in turn regressed to obtain the interpolation coefficients for equation (41). The data obtained from Baes and Mesmer (1976) consists of values of ΔG_f° and ΔH_f° for a few hydrolyzed species that are not listed in the U.S. National Bureau of Standards Technical notes. Again, these data are used to calculate values of $\log K_{eq}$ and ΔH_R° at 25°C. Additional values of $\log K_{eq}$ and ΔH_R° at 25°C, not obtainable from the previous sources, are taken from the original *PHREEQE* data base and from the *WATEQ* or *WATEQF* data bases. The final source of data which are not available from the previous sources is the data base for *SOLMNEQ* which consists of

$\log K_{eq}$ values for mineral dissociation reactions at specific temperatures between 0°C and 300°C. While a few values of $\log K_{eq}$ at 25°C are used directly, these data are primarily used to obtain interpolation coefficients required by equation (41).

The major modification made to *PHREEQE* was to allow simulations of mineral solubility reactions in brines by incorporating the Pitzer activity coefficient model into *PHREEQEX*. This alleviates the problems associated with applying an activity coefficient calculated by a single ion model in *PHREEQE* (i.e. Debye-Hückel, extended Debye-Hückel or Davies equations) to mineral solubility calculations. The improved version of *PHREEQEX* incorporating the Pitzer equations is referred to as *PHREEQEP*. To accompany *PHREEQEP*, two data bases of thermodynamic parameters are required. The first data base is essentially a version of the previous thermodynamic values for the species, minerals and gases. However, as will be discussed in the following pages, the number of species in this data base is reduced dramatically. The second data base consists of the thermodynamic parameters for the species with ion interaction parameters required by the Pitzer equations.

Because the Pitzer equations account for the formation of ion pairs as the salinity of a solution increases, the data base of aqueous species for the version of *PHREEQE* which includes the Pitzer equations require only the stoichiometric components. For example, the cations are Na^+ , K^+ , Ca^{+2} , Mg^{+2} , MgOH^+ , H^+ , Fe^{+2} , Sr^{+2} , Ba^{+2} , Li^+ and Al^{+3} ; the anions are Cl^- , Br^- , I^- , OH^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , HSO_4^- , and H_3SiO_4^- ; the neutral species include CO_2^0 and H_4SiO_4^0 . It should be noted that the specific ion interaction model only accounts for ion interaction due to increases in salinity and not due to changes in pH. The dissociation of a strong electrolyte, such as NaCl or CaCl_2 , is essentially complete in solutions of low salinities and their interaction is also virtually independent of changes in the pH of the solution at all salinities. However, weak electrolytes, such as H_2CO_3 and H_2SO_4 , or elements that readily undergo hydrolysis, such as aluminum and iron, dissociate into a series of species whose formation depends upon the pH of the solution and not its salinity.

Therefore, the data base must include these major aqueous components that will be dominant over the entire range of pH that could be encountered during a study. For example, the carbonate components included in the data base are CO_2^0 , HCO_3^- and CO_3^{2-} , and the aluminum components are Al^{+3} , $\text{Al}(\text{OH})^{+2}$, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_4^-$.

The data base of electrolyte parameters required by the Pitzer equations include the cation-anion interaction parameters $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and $C_{ca}^\dagger$, the cation-cation and anion-anion interaction parameters θ_{cc} and θ_{aa} , the triple interaction parameters ψ_{caa} and ψ_{acc} and the neutral species-ion parameters λ_{nc} and λ_{na} . All of the ion interaction parameters and the source of these data are listed in Appendix 1. The values contained within the data base are from a number of sources. Data are chosen in the following order of preference: (1) Harvie et al. (1984), (2) other mineral solubility studies, (3) electrolyte chemistry studies, and (4) my estimates. The preference for data is oriented towards the mineral solubility studies because this is the focus of this study. In general there is not much difference between the parameters determined from mineral solubility studies and those from electrolyte chemistry studies.

Unfortunately, data are not available for all the combinations of cation-anion pairs. While most of the ion pairs among the major components found in natural waters are represented by ion interaction parameters data for many ion pairs present in minor quantities have not been determined. Most of the missing data correspond to components which are present in relatively minor concentrations but are still geologically significant. This group of missing data also includes ions that are affected by hydrolysis reactions, where the form of the species is controlled by the pH of the solution. These species create a problem for the Pitzer equations because unlike strong electrolytes which completely dissociate symmetrically, the ion interaction parameters for hydrolyzed species can not be applied equally to the cation and anion. Thus, the hydrolyzed forms must be considered separately. In this data base, these pH dependent components include iron and aluminum (manganese does not readily hydrolyze in natural waters). The hydrolyzed

species of Fe and Al, which must be included in the data base, are Fe^{+2} , FeOH^+ , Al^{+3} , Al(OH)^{+2} , Al(OH)_2^+ and Al(OH)_3 . The missing values of the ion interaction parameters are estimated using similar cation-anion pairs for which data are known. The procedure for estimating these data is discussed in Chapter III. The activity coefficients of these species are calculated by using the distributing the mass among the species with mass balance equations (equation (1)) and the *Law of Mass Action* (equation (9)), and incorporating these masses into the Pitzer equations. This approach will allow the activity coefficient of the pH dependent species to be calculated with the Pitzer equations, and hence, estimates of the solubility of Al and Fe bearing minerals.

A second area where the data base of ion interaction parameters for the Pitzer equations is limited, concerns the species that undergo reduction or oxidation reactions. The species in this data base that commonly exist in natural waters as different oxidation states, and their oxidation states, are Fe(II) - Fe(III), Mn(II) - Mn(III), S(VI) - S(-II) and C(IV) - C(-IV). The oxidized state of the species is determined by the redox potential of the solution and not by the ionic strength. Currently, ion interaction parameters have been determined from experimental data for only half of the redox pair. These include the oxidized forms of carbon and sulphur (C(IV) and S(VI)) and the reduced forms of iron and manganese (Fe(II) and Mn(II)). Because ion interaction parameters for the pH dependent species of these oxidation states are known, these species are included in the data base, and are Fe^{+2} , FeOH^+ , Mn^{+2} , CO_2^0 , HCO_3^- and CO_3^{2-} , SO_4^{2-} , and HSO_4^- . Thus, the pH dependent species of the other oxidation states of the elements which are not included in the data base are Fe^{+3} , FeOH^{+2} , Fe(OH)_2^+ , Fe(OH)_3^0 , Fe(OH)_4^- , Mn^{+3} , MnO_4^- , MnO_4^{2-} , CH_4^0 , S^{-2} , HS^- and S^0 .

The pe and pH regions where calculations made with the data base will be accurate is illustrated by the shaded region in Figure 5. This region represents the pe - pH region where a system that contains all four components Fe, Mn, S and C co-exist. If a subsystem is chosen for study which contains fewer components, or only one, the area where valid

calculations can be made will be larger. For example, if a system is chosen which excludes sulphur and iron, the valid region would include all p_e - pH conditions to the left of the Mn line, above the C line and below the $P_{O_2} = 1$ atm line; an area twice as large as that when all four components are included.

The final set of values contained within the data base of ion interaction parameters for the Pitzer equations are coefficients for an interpolation function used to calculate values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $C^\dagger$ from 0°C to 200°C (Table A.8). The form of the interpolation function, the coefficients and the sources of the data used to derive these interpolation coefficients are discussed in detail in the following chapter.

The data base of the ion interaction parameters is coded in a manner which will easily facilitate changes to the current values and allow new values to be added. Values for each of the cation-anion parameters ($\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and $C_{ca}^\dagger$) are entered as a separate matrix with rows representing the cation member and the columns representing the anion member of the ion pair. The cation-cation and anion-anion parameters (θ_{cc} and θ_{aa}) are also listed as matrices with the rows and columns referring to the first and second ions, respectively. Because the values of these two parameters for the interaction of ion "a" with ion "b" is the same as the interaction of ion "b" with ion "a", these matrices form a mirror image along their diagonal of ion "a" with ion "a". Values of the triple ion parameters (ψ_{caa} and ψ_{acc}) are entered slightly differently. These values are entered as rows, with the first two numbers in a row identifying the two cations and the remaining values in the row corresponding to the ion interaction parameters for each anion in the data base. For example, one row could represent the values for $\psi_{Na,K,Cl}$, ψ_{Na,K,SO_4} , ψ_{Na,K,H_2SO_4} , ψ_{Na,K,CO_3} , etc. The next row would represent $\psi_{Na,Ca,Cl}$, ψ_{Na,Ca,SO_4} , ψ_{Na,Ca,H_2SO_4} , ψ_{Na,Ca,CO_3} , etc. The neutral species-ion parameters (λ_{nc} and λ_{na}) are entered as matrices in a similar manner to the cation-anion parameters. Finally, the coefficients for the function which interpolates values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $C^\dagger$ from 0°C to 200°C are coded as four lines for each ion pair. The first line contains the ion

pair identifier and the four coefficients for $\beta^{(0)}$. The subsequent three lines contain the four coefficients for $\beta^{(1)}$, $\beta^{(2)}$ and C^* .

An inconvenience with models such as *PHREEQE* is that they have been designed to run on a mainframe computer. Two new versions of *PHREEQE*, one without the activity coefficient model based upon the Pitzer equations, and one which incorporates the Pitzer equations, were optimized to run on an IBM personal computer. This modification eliminates the high cost of using mainframe computers and increases the versatility and portability of the geochemical code. These two new codes are personal computer versions of *PHREEQEX* and *PHREEQEP* and are called *PC-PHREEQEX* and *PC-PHREEQEP*, respectively. The same data bases used by the mainframe versions of the model are used by the respective personal computer versions.

In summary, four improved versions of *PHREEQE* have been prepared:

- PHREEQEX* : a mainframe version without the Pitzer equations;
- PHREEQEP* : a mainframe version with the Pitzer equations;
- PC-PHREEQEX* : a personal computer version without the Pitzer equations;
- PC-PHREEQEP* : a personal computer version with the Pitzer equations.

Three sets of simulations were undertaken with the various versions of *PHREEQE* to compare execution times for runs on a mainframe computer and on a personal computer. The codes designed for the micro computers are compiled with the IBM Professional FORTRAN Compiler (version 1.23) on the three IBM compatible personal computers. Only one mainframe computer is used during this study, a CYBER, and the codes are compiled with the C.D.C. NOS/VE version of FORTRAN. The scenarios include a sea water speciation problem and two gypsum solubility scenarios. The latter two scenarios represent solubility in a 0.05 m_{NaCl} solution and a 3.00 m_{NaCl} solution. The sea water speciation problem is designed to account for the distribution of dissolved mass from 25 elements among 220 species and calculate the saturation indexes of 42 minerals. This problem can be undertaken only with the two versions of *PHREEQEX* and *PC-*

PHREEQEX because the Pitzer equations versions of *PHREEQE* require a data base of stoichiometric components rather than a data base comprised of specific species. Hence, the two data bases of species are very different. The simulations which determine the solubility of gypsum in NaCl solutions are run at 25°C. When the solution has a salinity of 3.0 m_{NaCl}, the single ion activity coefficient models used in *PHREEQEX* and *PC-PHREEQEX* would result in an incorrect estimate. Hence, at this salinity, the solubility of gypsum can be accurately simulated only with *PHREEQEP* and *PC-PHREEQEP*.

A numerical evaluation of the integrals within the $J(x)$ and $J'(x)$ functions used to calculate the higher order electrostatic terms Θ_{ij} and Θ'_{ij} (equations (39) and (40)) is required. The technique used to evaluate the integrals in *PHREEQEP* and *PC-PHREEQEP* is known as Romberg integration and a subroutine that will undertake this task is taken from Gerald (1978). Because numerical integration is very time consuming, a simpler expression to solve for $J(x)$ which approximates the integral is used here. The approximating function for $J(x)$, taken from Pitzer (1975), and its first derivative are:

$$J(x_{ij}) = \frac{x}{\left(4.0 + c_1 \cdot \frac{e^{-c_3 \cdot x^{c_4}}}{x^{c_2}}\right)} \quad (43)$$

$$J'(x_{ij}) = \frac{4.0 + c_1 \cdot \frac{e^{-c_3 \cdot x^{c_4}}}{x^{c_2}} (1.0 - c_3 c_4 x^{c_4} + c_2)}{\left(4.0 + c_1 \cdot \frac{e^{-c_3 \cdot x^{c_4}}}{x^{c_2}}\right)^2} \quad (44)$$

where: c_1, c_2, c_3, c_4 = regression coefficients (from Pitzer, 1975)

Because *PHREEQEP* and *PC-PHREEQEP* contain subroutines which calculate $J(x)$ and $J'(x)$ by both the integral expression and the approximating function, the user may choose which method to use to evaluate $J(x)$ and $J'(x)$. Numerous simulations undertaken using both techniques show a negligible loss of accuracy when applying the approximating

function. The integral expression is included in the code should the user desire more accuracy in the calculations than can be obtained using the approximating function.

The times required to run these three scenarios on the mainframe and personal computers are listed in Table 2.2. The execution times for simulations are greater on the personal computer than on a mainframe computer, yet not prohibitively so. For example, typically, the maximum times incurred with the personal computers are in the order of approximately 5-10 minutes for the gypsum solubility simulations. However, using the approximating function for calculating the values of $J(x)$ and $J'(x)$ reduces these execution times by approximately 95%.

VERIFICATION OF THE GEOCHEMICAL MODEL

Calculations of the solubility of gypsum and calcite in a Na-Cl brine at 25°C are presented by Figure 6 to illustrate the accuracy of the specific ion interaction model coupled to a speciation and mineral stability code. The analyses use *PC-PHREEQEP* and *PC-PHREEQEX*. Simulations with the latter code are undertaken with three different thermodynamic data bases of species:

- free ions* : the free ion;
- all species* : all species including free ions, ion pairs and neutral species;
- charged species* : all free ions and ion pairs, but excluding neutral species.

It is evident that only the geochemical code incorporating the Pitzer equations can accurately reproduce the experimental data for gypsum over the entire range of salinity. Because the Pitzer equation model is a specific ion interaction model, this technique accounts for ion pairing within the solution and is able to determine the amount of the free ions which are available for the mineral solubility reaction (e.g. Ca^{+2} and SO_4^{2-} for gypsum). While the fit between the simulated and experimental data for calcite is not as good as that for gypsum, the fit is still considerably better than that obtained from the code

Table 2.2: Execution times for simulations run with the improved versions of *PHREEQE*.

version of <i>PHREEQE</i>	computer ²	sea water speciation	simulations ¹			
			solubility of gypsum ⁶			
			in 0.05 m _{NaCl}	in 0.05 m _{NaCl}	in 3.00 m _{NaCl}	in 3.00 m _{NaCl}
			integral ³	approx ³	integral ³	approx ³
<i>PHREEQEP</i>	CYBER	----- ⁴	98 s	6 s	98 s	6 s
<i>PC-PHREEQEP</i>	PC	----- ⁴	697 s	47 s	612 s	47 s
	AT	----- ⁴	626 s	24 s	616 s	24 s
	COM	----- ⁴	338 s	19 s	337 s	19 s
integral ³ and approx ³ not applicable						
<i>PHREEQEX</i>	CYBER	10 s		9 s		----- ⁵
<i>PC-PHREEQEX</i>	PC	90 s		81 s		----- ⁵
	AT	49 s		44 s		----- ⁵
	COM	32 s		29 s		----- ⁵

NOTES:

1: see text for a discussion of these simulations.

2: computers: PC : IBM PC with 8087-3 co-processor and IBM DOS 3.10.
 AT : IBM AT with 80286 co-processor and IBM DOS 3.20.
 COM : COMPAQ DESKPRO 286 with 80286 co-processor and COMPAQ DOS 3.31.
 CYBER : CYBER 830 mainframe computer, NOS/VE 1.3.1 operating system.

3: integral: Pitzer equations include an integral expression to calculate $J(x)$ and $J'(x)$.
 approx: Pitzer equations include an approximating function to calculate $J(x)$ and $J'(x)$.

4: not run because species data base is not applicable to Pitzer equation based models.

5: not run because results would not be accurate with codes using Debye-Hückel equations.

6: all gypsum solubility simulations run with the initial $m_{\text{CaSO}_4} = 0.055$.

with the single ion activity coefficient model. These two minerals were chosen to illustrate that while the solubility of most minerals are reproduced very well by *PC-PHREEQEP*, there is still some refining of parameters required for the carbonate minerals. Harvie and Weare (1980) and Harvie et al. (1984) also simulated the solubility of gypsum and calcite with a mineral solubility code incorporating the Pitzer equations and it predicted similar results.

The calculated solubility of minerals using *PC-PHREEQEX* is less satisfactory at high salinities because the theory for single ion activity coefficient models is invalid at such concentrations. In addition, solubility calculations with *PC-PHREEQEX* are very dependent upon the data base of aqueous species. This can lead to two significant problems. First, mass will be distributed only among the ion pairs chosen by the modeller. All of the ion pairs that exist in brines may not be included in the data base. Second, with so many ion pairs in brines, thermodynamic data for all required species may not be available or, if available, the values may not be accurate. These problems can be illustrated by modelling the solubility of gypsum and calcite with *PC-PHREEQEX*. The first simulation (Figure 6, "only free ions" curve) uses just the *free ion* data base (i.e. for the gypsum simulation this consists of the ions Na^+ , H^+ , Ca^{+2} , Cl^- , OH^- , SO_4^{2-}). In this example it is assumed that all of a given component, such as Na, is present as the free ion. The calculated solubility of gypsum generally follows the trend of the experimental data, but the actual values are substantially lower. This result is expected because the simulation did not consider the ion pairs that form in brines.

The next simulation combines *PC-PHREEQEX* and the charged species data base. For example, the species in this data base which are considered for the dissolution of gypsum in a NaCl solution are Na^+ , NaSO_4 , Ca^{+2} , CaOH^+ , H^+ , OH^- , Cl^- , SO_4^{2-} and HSO_4^- . The accuracy of the predicted solubility of gypsum (Figure 6, "no neutral species" curve) improves slightly from the previous simulation because the formation of ion pairs reduces the amount of free ions and hence increases the solubility of the mineral.

Finally, *PC-PHREEQEX* was run with the *all species* data base (Figure 6, "all species" curve). The ions and ion pairs which represent a NaCl solution which contains dissolved gypsum are Na^+ , NaCl^0 , NaOH^0 , NaSO_4^- , Na_2SO_4^0 , Ca^{+2} , CaCl_2^0 , CaOH^+ , $\text{Ca}(\text{OH})_2^0$, H^+ , OH^- , Cl^- , HCl^0 , SO_4^{2-} and HSO_4^- . This data base contains many of the ion pairs that the Pitzer equations should consider. However a special problem occurs due to the presence of neutral species in the data base. Because the Debye-Hückel and the Davies equations are designed for charged species, *PHREEQE*, as well as other geochemical codes, has an expression which calculates the activity coefficient of neutral species as a function of the ionic strength ($\log \gamma = 0.1 \times I$). This procedure causes excessively large amounts of mass to be concentrated in the form of neutral species. Hence, the calculated mineral solubility is overestimated dramatically as salinity increases. Harvie and Weare (1980) have shown similar trends when the solubility of gypsum in brines is estimated with the geochemical codes *SOLMNEQ* and *WATEQF*.

The results of these simulations demonstrate the need for incorporating a specific ion interaction model, such as the Pitzer equations, into a geochemical modelling code when mineral solubility studies are simulated in very saline solutions. In addition, inaccuracies in the calculated solubilities that result from the data base of species are eliminated when using the Pitzer ion interaction model because this technique does not require a complete set of every free ion, charged ion pair and neutral species that exists in a brine.

CONCLUSIONS

Geochemical modelling codes have applications to hydrogeological studies because they can be used to predict which minerals will dissolve and which will precipitate under various hydrogeological conditions. When these changes occur, the structure of the porous media is altered. While several such codes are currently available, they are typically limited in their application to hydrogeological systems. These limitations typically include:

1. the maximum salinity to which the codes can accurately simulate reactions is approximately 6000 mg/L NaCl (ionic strength of 0.1);
2. the number of species (especially ion pairs and neutral species) in the data base are limited;
3. most thermodynamic data for the species were measured at 25°C and extrapolations to higher temperatures are only approximate in many cases;
4. most existing codes typically are designed to use expensive, large mainframe computers;

The major concern with simulations of brines is that a considerable amount of dissolved mass may exist as ion pairs whereas most of the dissolved mass in fresh water exists as free ions. In theory, the inclusion of a data base comprising all ion pairs which exist in brines should improve the accuracy of the calculations. However, knowing which species are present and obtaining accurate thermodynamic values for these species is a very difficult task. The second major limitation of the present codes concerns one of the major parameters influencing the simulation of transfer of mass among solid phases and species; the activity coefficient. Currently most geochemical codes incorporate a single ion model such as the Debye-Hückel or Davies equations for calculating the activity coefficients. However, because the theory upon which the single ion models is based is not valid for very saline systems, the calculated activity coefficients and mineral solubilities are not accurate. A specific ion interaction model, such as the Pitzer equations, accounts for both the interaction of ions in saline solutions and the electrostatic changes that occurs within a solution as its salinity increases. Rather than calculate an activity coefficient for a single ion, the Pitzer equations calculate a stoichiometric activity coefficient for a given component in the solution. Thus a geochemical modelling code which incorporates the Pitzer equations can accurately calculate mineral solubilities in solutions of any ionic strength.

The research presented here has removed the above restrictions associated with applying the current geochemical models to simulations of mineral solubility which occur

in deep sedimentary basins. This is accomplished by modifying an existing geochemical code, known as *PHREEQE*. Specific improvements include:

1. the specific ion interaction model for calculating activity coefficients developed by Pitzer and co-workers has been incorporated into *PHREEQE* to enable it to simulate mass transfer among aqueous components and minerals in very saline groundwater;
2. a comprehensive data base of equilibrium constants for mineral dissolution reactions and of ion interaction parameters required by the Pitzer equations, both to 200°C, has been compiled;
3. by using the Pitzer equations, which calculate stoichiometric activity coefficients and account for the effects of ion pairing, a complete data base of thermodynamic values for all ions pairs which may exist in brines is not required; only the stoichiometric components found in a solution are required for mineral stability reactions;
4. the code with the Pitzer equation activity coefficient model has been programmed for an IBM personal computer, thus optimizing costs and increasing the versatility of *PHREEQE*.

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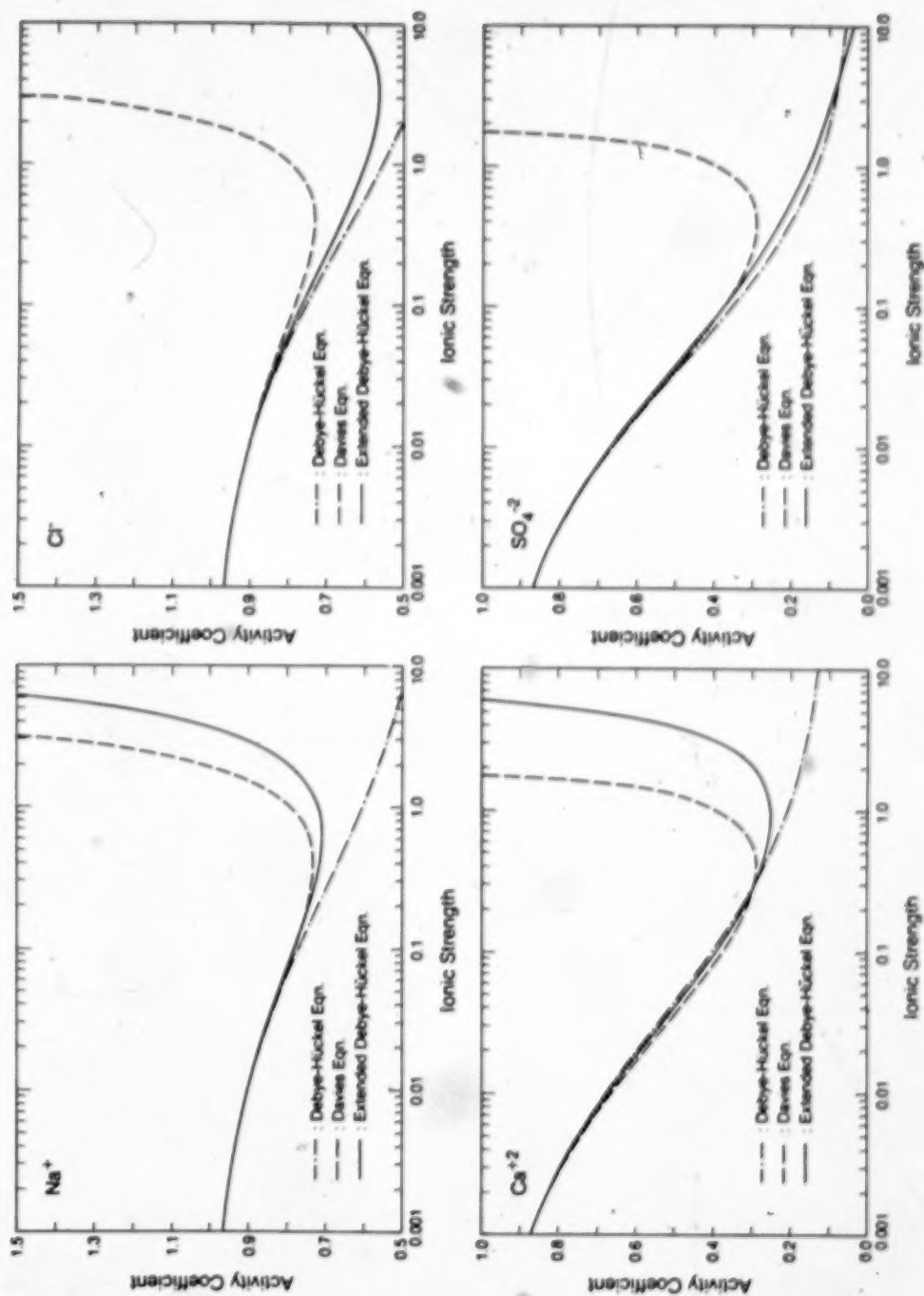


Figure 1. Activity coefficients of Na⁺, Cl⁻, Ca⁺², and SO₄⁻², calculated by a single ion activity coefficient model, as a function of ionic strength of a solution based on seawater.

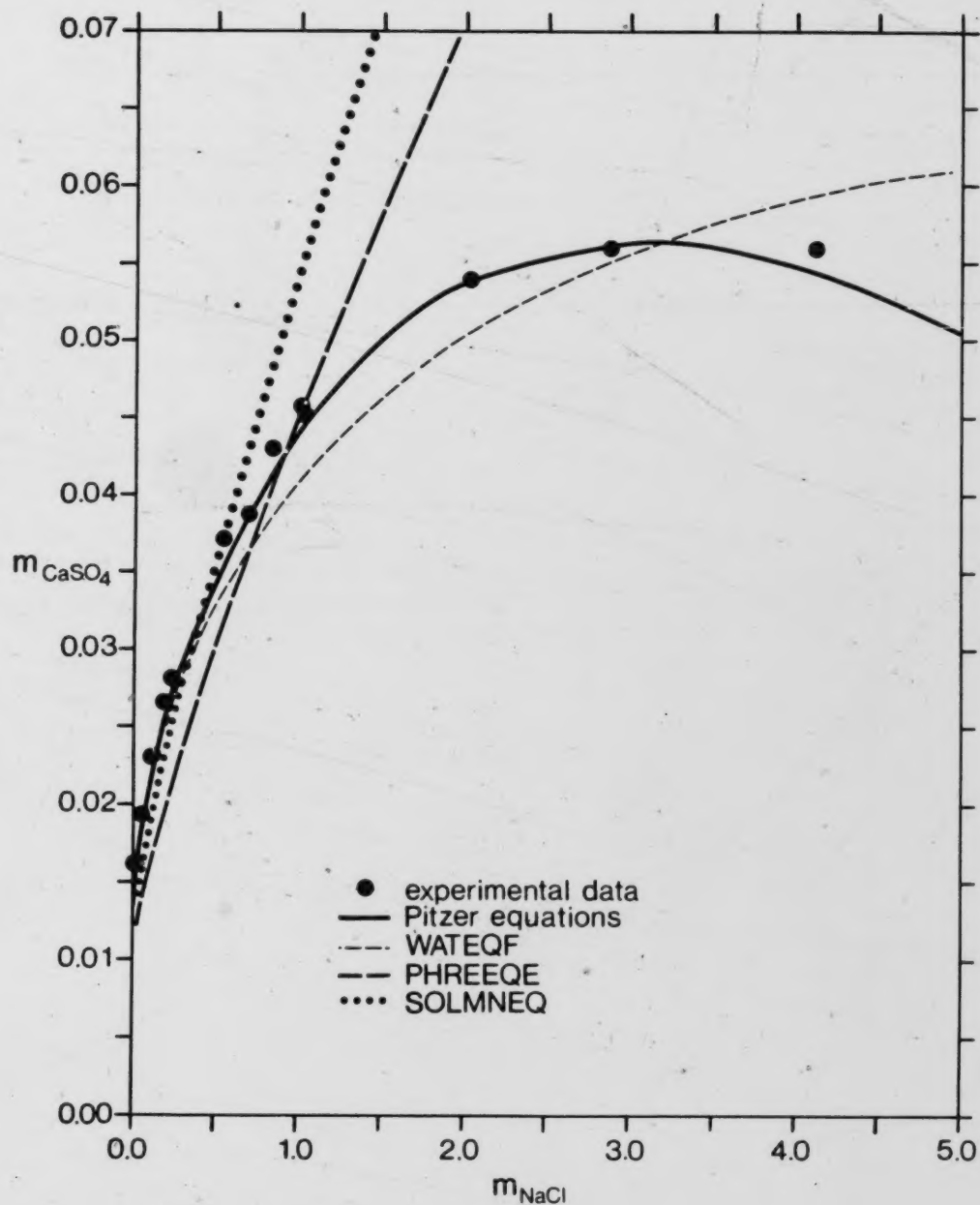


Figure 2. Solubility of gypsum as estimated by various geochemical codes.

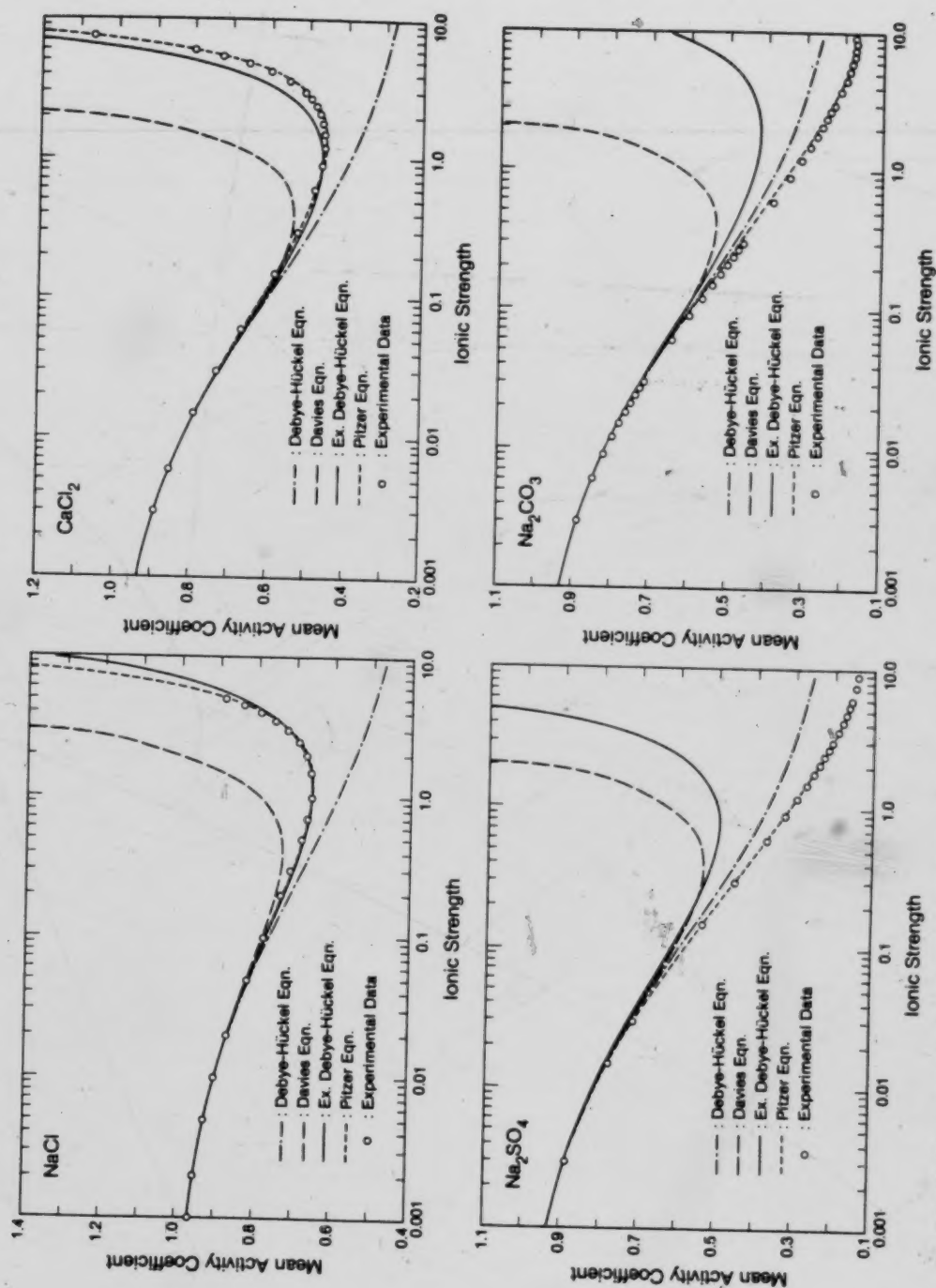


Figure 3. Comparison of calculated and experimentally determined mean activity coefficients of NaCl, CaCl₂, Na₂SO₄ and Na₂CO₃ in pure H₂O.

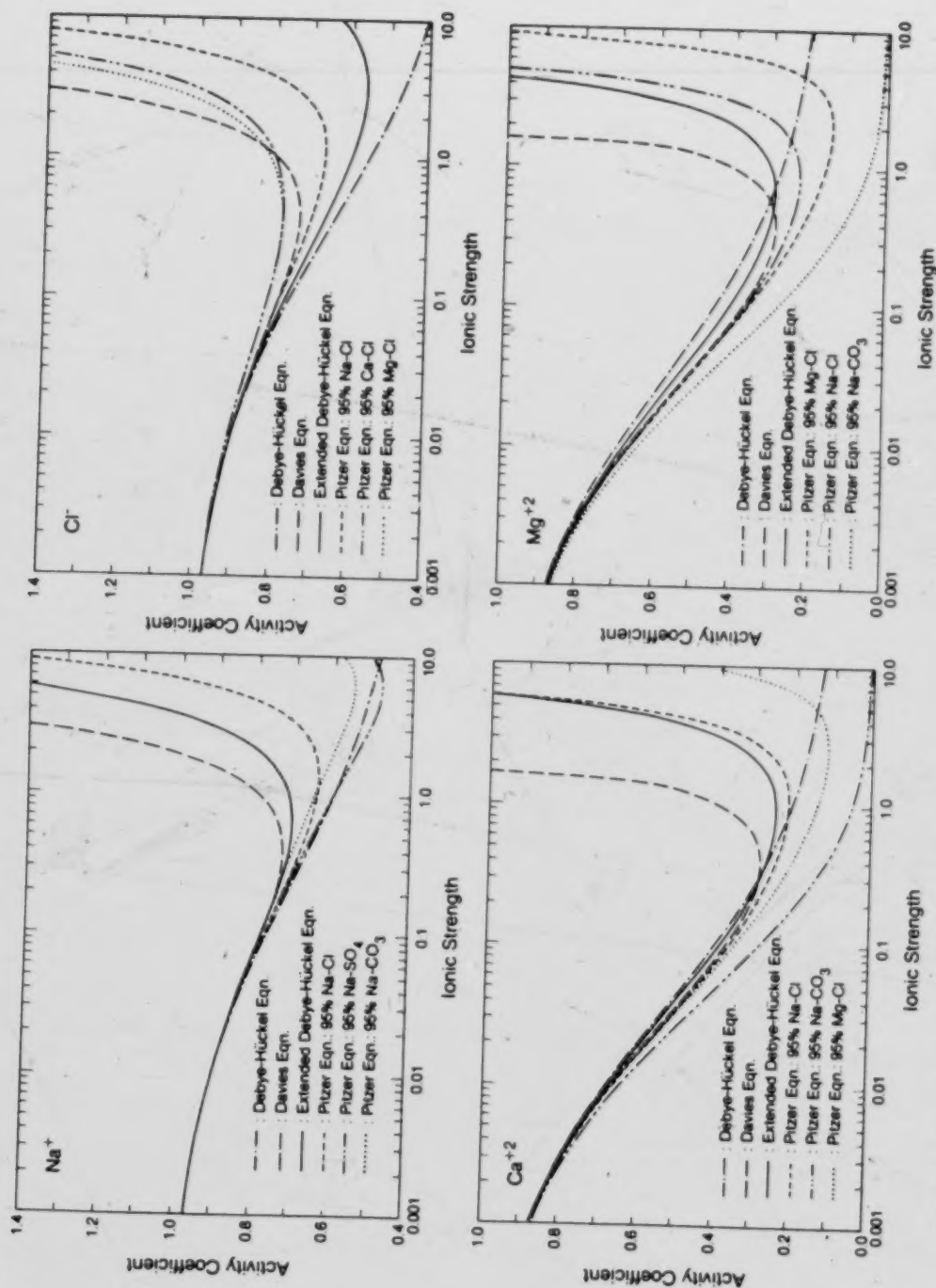


Figure 4. Activity coefficients of Na⁺, Cl⁻, Ca²⁺, and Mg²⁺, calculated by single ion and specific ion interaction models, for solutions of various chemical compositions.

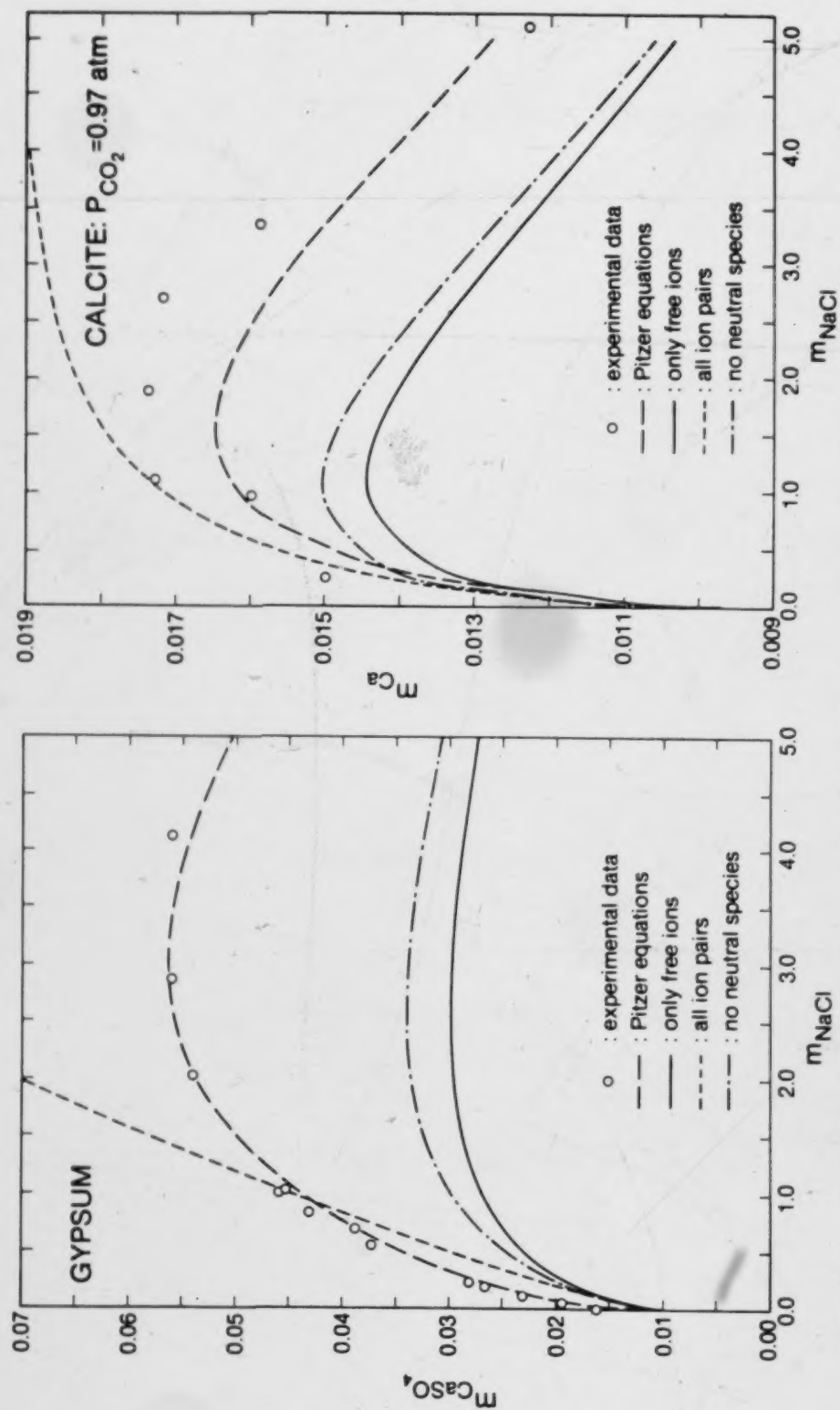


Figure 5. Calculated and experimentally determined solubilities of gypsum and calcite in a Na-Cl solution varying from $m_{\text{NaCl}} = 0.0$ to 5.0.

III. ESTIMATION OF ION INTERACTION PARAMETERS FOR THE PITZER EQUATIONS AT 25°C AND FROM 0°C TO 200°C

INTRODUCTION

Numerical modelling techniques based upon aqueous geochemical and thermodynamic principles have proven invaluable for studying water-rock interactions within a variety of geological environments. These computer codes can be used to describe the dissolution and precipitation of minerals, as well as the speciation of dissolved components. Examples of these geochemical codes include *SOLMNEQ* (Kharaka and Barnes, 1973), *WATEQF* (Plummer et al., 1976), *MINEQL* (Westall et al., 1976), *EQ3/EQ6* (Wolery, 1979) and *PHREEQE* (Parkhurst et al., 1980). Due to the thermodynamic theory upon which these models are based, they are typically accurate only in relatively fresh water systems. The major limitation with applying the current geochemical codes to saline waters or brines relates to the portion of the code which calculates the activity coefficients of the aqueous species. The technique used is a critical component of the model because the activity coefficient strongly influences the calculations which distribute mass as either minerals or aqueous species. These codes use a single ion model such as the Debye-Hückel, the extended Debye-Hückel or the Davies equations to calculate an activity coefficient. Because of the increasingly significant effects of ion interactions as the solution becomes more saline, the theory upon which these equations are based becomes invalid at high salinities and the calculated mineral solubilities are inaccurate.

A recent technique developed by Pitzer and his co-workers (Pitzer, 1973, 1975, Pitzer and Mayorga, 1973, 1974, Pitzer and Kim, 1974, Silvester and Pitzer, 1977, 1978) has extended our ability to predict values of the activity coefficient of electrolytes or ions in solutions with salinities ranging from that of fresh water to brines. The Pitzer equations are a specific ion interaction model, and thus accounts for the effects of all ions in solution.

There are advantages to using the Pitzer equations for geochemical modelling in addition to their ability to accurately calculate activity coefficients in very saline solutions. These include their ability to be efficiently adapted into existing computer codes because the equations require relatively few ion interaction parameters, and these parameters are available for a multitude of cation-anion pairs.

The Pitzer equations have been successfully applied to a number of geological studies involving mineral stability in saline solutions or brines and to speciation in sea water (Whitfield, 1975a, 1975b, Harvie and Weare, 1980, Harvie et al., 1982, 1984, Gueddari et al., 1983, Monnin and Schott, 1984, Brantley et al., 1984). However, these studies were conducted at or near 25°C. The main reason for the lack of studies at temperatures other than 25°C is that the high temperature values of the ion interaction parameters required by the Pitzer equations are typically not available. While there are considerable data at 25°C, high temperature data are generally limited to relatively few cation-anion pairs or to temperatures not far from 25°C. Interpolation functions for estimating the parameters required by the Pitzer equations at high temperatures are available for only several ion pairs. However, the mathematical framework of these equations is normally very complex and varies from study to study, making the collective use of these equations in geochemical codes awkward.

Pabalan and Pitzer (1987) successfully demonstrated the applicability of the Pitzer ion interaction model to the calculation of mineral equilibria in brines at high temperatures. However, because their study is based upon the existing published ion interaction data at high temperatures, their work is focused upon the limited system Na-K-Mg-Cl-SO₄-OH and this study did not examine systems in which the temperature is below 25°C. In addition, the high temperature interpolation equations used in their study to interpolate the ion interaction parameters to high temperatures are the same as in the original paper. Thus, their model is not part of a general mineral-solution equilibrium model, nor can be readily incorporated into one.

This chapter addresses the problems associated with both the lack of values for ion interaction parameters at temperatures other than 25°C and the lack of standardization of the interpolation functions that currently exist. Specifically, the objectives of this chapter are to (1) develop a technique for estimating the ion interaction parameters required by the Pitzer equations, at 25°C, which currently do not exist in the published literature, (2) develop a technique for obtaining high temperature values required by the Pitzer equations over the temperature range of 0°C to 200°C which also have not been determined, and (3) develop a single, yet simple, interpolation function, suitable for inclusion into existing geochemical codes, that will accurately reproduce the ion interaction parameters from 0°C to 200°C that are currently calculated by the existing published interpolation models and will be estimated as part of this study. The main reasons for developing a simpler equation, rather than using the existing more complex formulae, are that a simple and consistent interpolation equation comprised of only three or four interpolation coefficients is much easier to program in a geochemical code and the data base of required interpolation coefficients can easily be compiled. An upper limit of 200°C is chosen because this temperature is an appropriate upper limit of diagenetic reactions in deep sedimentary basins. A lower limit of 0°C is chosen because most near-surface groundwater systems are typically at temperatures between 0°C and 25°C.

THE CURRENT DATA BASE OF ION INTERACTION PARAMETERS

Ion interaction parameters of interest in this study are the cation-anion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ . Values of these parameters have been compiled for a considerable number of cation-anion pairs at 25°C (Pitzer and Mayorga, 1973, 1974, Pitzer, 1979, Harvie and Weare, 1980, Harvie et al., 1984). The present study concentrates on a smaller data base comprised of some of the chemical components which are important in natural waters. These include the alkali elements (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), the alkali earth metals (Be^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2}), and the anions Cl^- and SO_4^{2-} . Even

though the anionic species CO_3^{2-} is geologically important, it is not discussed here because there are insufficient experimentally determined values of the ion interaction parameters at temperatures well above 25°C. However, because of the similar chemical properties between CO_3^{2-} and SO_4^{2-} , estimates for the CO_3^{2-} can be obtained from the SO_4^{2-} values. Also, the terms θ and ψ are not considered here because the variation of these parameters with temperature is negligible when the temperature change is less than 100°C (Phutela and Pitzer, 1986b). A more recent study of mineral-brine equilibria by Pabalan and Pitzer (1987) showed that the application of the Pitzer equations, with values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ varying with temperature, but with values of θ and ψ either constant with temperature or exhibiting simple dependence, exhibited a good representation of the experimental data. Hence, accounting for the variations of these two parameters with temperature will contribute minimally to the accuracy of the mineral solubility calculations.

A review of the literature containing the high temperature values of ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ reveals that these data can be divided into three groups. The first group of parameters are individual values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ which have been determined at a specific temperature (e.g. at 110°C). Table 3.1 lists publications which provide data in this form.

The second type of data describes the change of an ion interaction parameter with temperature when the temperature is not far above 25°C. For example, this relation is typically expressed as:

$$\frac{\partial Y}{\partial T} = c \quad (22)$$

where: Y = one of the ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ or C^ϕ
 T = the temperature of interest (K)
 c = the slope of the change of a parameter with temperature

or, in the integrated form:

Table 3.1: Published sources of high temperature values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^* .

	REFERENCE	MAX m	TYPE AND RANGE OF DATA
LiCl	Holmes and Mesmer (1983a) *	6.0	interpolation functions, 0 to 250°C
	Holmes and Mesmer (1981b)	6.0	values at 110, 139, 171, 200°C
NaCl	Silvester and Pitzer (1977) *	6.0	interpolation functions, 0 to 300°C
KCl	Holmes and Mesmer (1983a) *	6.0	interpolation functions 0 to 250°C
	Conti et al. (1986)	9.0	interpolation functions, 60 to 250°C
	Holmes et al. (1978)	6.0	values at 109, 141, 172, 201°C
CsCl	Holmes and Mesmer (1983a) *	6.0	interpolation functions, 0 to 250°C
	Saluja et al. (1986)	1.0	interpolation functions 25 to 100°C
	Holmes and Mesmer (1981b)	8.0	values at 110, 139, 171, 200°C
HCl	Ruaya and Seward (1987) *	3.0	interpolation functions, 25 to 350°C
	Tremaine et al. (1986)	1.0	interpolation functions, 10 to 140°C
	Saluja et al. (1986)	0.4	interpolation functions 25 to 100°C
CaCl ₂	Phutela et al. (1987) *	1.0	interpolation functions, 0 to 200°C
	Phutela and Pitzer (1983)	5.0	interpolation functions 25 to 175°C
	Kumar (1986)	6.4	interpolation functions, 50 to 200°C
	Ananthaswamy and Atkinson (1985)	9.0	interpolation functions 0 to 100°C
	Holmes et al. (1978)	6.0	values at 109, 141, 172, 201°C
MgCl ₂	Phutela et al. (1987) *	1.0	interpolation functions, 0 to 200°C
	de Lima and Pitzer (1983)	7.0	interpolation functions 25 to 200°C
	Holmes et al. (1978)	6.0	values at 109, 141, 172, 201°C
BaCl ₂	Holmes and Mesmer (1981a)	?	values at 110, 140, 171, 200°C
SrCl ₂	Phutela et al. (1987) *	1.0	interpolation functions, 0 to 200°C
	Holmes and Mesmer (1981a)	?	values at 110, 140, 171, 200°C
Na ₂ SO ₄	Holmes and Mesmer (1986b) *	3.0	interpolation functions, 0 to 225°C
	de Lima and Pitzer (1983)	2.5	interpolation functions 25 to 300°C
	Rogers and Pitzer (1981)	2.5	interpolation functions 25 to 200°C
	Bhatnagar and Campbell (1981)	1.8	values at 50, 75, 100, 125, 150°C
	Bhatnagar and Campbell (1982)	1.8	values at 150, 175, 200, 225, 250°C
	Holmes and Mesmer (1986a)	?	values at 110, 140, 170, 225°C
K ₂ SO ₄	Holmes and Mesmer (1986b) *	3.0	interpolation functions, 0 to 225°C
	Conti et al. (1986)	1.6	interpolation functions, 60 to 250°C
	Holmes and Mesmer (1986a)	?	values at 110, 140, 170, 225°C
Li ₂ SO ₄	Holmes and Mesmer (1986b) *	3.0	interpolation functions, 25 to 225°C
	Holmes and Mesmer (1986a)	?	values at 110, 140, 170, 225°C
Cs ₂ SO ₄	Holmes and Mesmer (1986b) *	6.0	interpolation functions, 25 to 225°C
	Holmes and Mesmer (1986a)	6.0	values at 110, 140, 170, 200°C
MgSO ₄	Phutela and Pitzer (1986a) *	2.0	interpolation functions, 25 to 200°C
	Holmes and Mesmer (1983b)	4.5	interpolation functions 25 to 110°C

* : interpolation functions used to obtain values of the ion interaction parameters for this study

$$Y(T) = Y(T_R) + c[T - T_R] \quad (23)$$

where: $Y(T)$ = the value of the parameter at the temperature of interest
 $Y(T_R)$ = the value of the parameter at the reference temperature
 T_R = the reference temperature (298.15K)

Values of the constant "c" for many ion pairs were determined by Silvester and Pitzer (1978) and later re-evaluated by Phutela and Pitzer (1986b). Because these constants represent a linear change of the ion interaction parameter with temperature, this expression is typically valid from 25°C to a maximum temperature of approximately 50°C.

The third source of published high temperature values of the parameters for the Pitzer equations is interpolation equations that express the ion interaction parameters as a function of temperature. The range of temperatures through which these interpolation equations are valid is normally large (e.g. from 0°C to 300°C for NaCl). These expressions are based upon a fit of experimentally determined values of the activity or osmotic coefficients, and exhibit in a variety of forms, from simple algebraic expressions to complex differential equations. A summary of the cation-anion pairs that have ion interaction parameters interpolated to high temperature with functions, and the maximum temperature to which these expressions can accurately be used, is given in Table 3.1.

The variations of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ with temperature for the chloride and sulphate anionic groups are illustrated by Figures 1 and 2, respectively. The source of the high temperature values of the ion interaction parameters that are used in this study is primarily obtained from published interpolation expressions. These functions were chosen over the slopes of the ion interaction parameters versus temperature because the latter values are generally inaccurate at temperatures above 50°C. Individual values, which are calculated at a specific temperature, typically do not have a sufficient number of points to produce a satisfactory regression over a large temperature range. The published interpolation

equations that were used to calculate the values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^* from 0°C to 200°C for this study are given in Table 3.1 and listed in Appendix 4.

ESTIMATION OF ION INTERACTION PARAMETERS

A Consistent Interpolation Equation to 200°C

An examination of the equations listed in Appendix 4 shows the variety of forms of published interpolation functions. Designing a computer code which can incorporate all of these interpolation equations and efficiently accommodate new equations for other ion pairs as they become available is difficult because each ion pair appears to require its own unique set of functions. If a standard interpolation function were developed, the incorporation of such an expression into a geochemical code and the construction of a data base comprised of the required interpolation coefficients would be facilitated quite simply. Requirements for an interpolation function that would be generally applicable to complex geochemical systems and yet relatively easy to incorporate into a geochemical model are:

1. the form of the interpolation equation must be standard among all ion interaction parameters and among all cation-anion pairs;
2. the expression should be a function of temperature only;
3. the equation should have a 25°C intercept value which is equal to the value of the ion interaction parameter at 25°C;
4. the interpolation function should contain no more than four interpolation coefficients;
5. the function should be accurate over the temperature range of 0°C to 200°C.

The values of the interpolation functions should have a 25°C intercept equal to the value of the particular ion interaction parameter at 25°C because in the vast majority of cation-anion pairs this is the only value which is known. Hence, a interpolation function can use this value as a starting point for the high temperature estimates. An equation which

is a function of only temperature would further enhance the simplicity of the equation. A function consisting of only a few interpolation coefficients could be reasonably accessed by the code and efficiently stored in a data base.

Fourteen different equations satisfying the above requirements selected for further evaluation are listed in Table 3.2. Four of these equations contain only two interpolation coefficients; six contain three coefficients and four equations contain four interpolation coefficients. In general, the terms of the proposed interpolation functions are the value of the ion interaction parameters at 25°C ($Y(T_R)$) and various combinations of differences between the temperature of interest and the reference temperature ($Y(T) - Y(T_R)$). The latter terms are either first, second or third order polynomials, first order reciprocal or logarithmic.

Values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ at temperature intervals of 25°C from 0°C to 200°C for thirteen Cl^- and SO_4^{2-} ion pairs are calculated using most of the published interpolation functions listed in Appendix 4. However, the functions for HCl , Li_2SO_4 , Cs_2SO_4 and MgSO_4 are valid only between 25°C and 200°C. In these four cases the values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ are estimated by visual extending the plot of the parameter versus temperature to 0°C. All values are refit by all the functions listed in Table 3.2 to obtain the interpolation coefficients. The standard errors of fit between the values obtained from the published interpolation curves and the proposed interpolation functions is also calculated to determine the accuracy of the new interpolation functions. The lowest calculated standard error of fit corresponds to the interpolation equation which best reproduces the values calculated with a published interpolation function. In addition to the ion interaction parameters obtained from the published equations, values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ for BaCl_2 are available at specific temperatures (110°, 140°, 171°, 200°C) from Holmes and Mesmer (1981a). These data were supplemented by Holmes and Mesmer (1981a) with data at 25°C from Pitzer and Mayorga (1973). Again the equations from Table 3.2 are used to fit these data.

Table 3.2: Proposed equations for interpolating $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^Φ to 200°C.

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] \quad (24)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^3 - T_R^3] \quad (25)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^1 - T_R^1] \quad (26)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[\ln T - \ln T_R] \quad (27)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^3 - T_R^3] \quad (28)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^1 - T_R^1] \quad (29)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[\ln T - \ln T_R] \quad (30)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^3 - T_R^3] + c[T^1 - T_R^1] \quad (31)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^3 - T_R^3] + c[\ln T - \ln T_R] \quad (32)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^1 - T_R^1] + c[\ln T - \ln T_R] \quad (33)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^3 - T_R^3] + d[T^1 - T_R^1] \quad (34)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^3 - T_R^3] + d[\ln T - \ln T_R] \quad (35)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^1 - T_R^1] + d[\ln T - \ln T_R] \quad (36)$$

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^3 - T_R^3] + c[T^1 - T_R^1] + d[\ln T - \ln T_R] \quad (37)$$

where: $Y(T)$ = ion interaction parameter $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^Φ at the temperature of interest

$Y(T_R)$ = ion interaction parameter at the reference temperature (25°C)

T = temperature of interest (°C)

T_R = reference temperature 25°C

a, b, c, d = interpolation coefficients

A more accurate method of choosing the interpolation function involves re-fitting the original experimental data (i.e. osmotic coefficients, activity coefficients, enthalpy, etc.) reported in Table 3.1. However, because the values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ calculated with the original equations (Appendix 4) accurately reproduce the experimental data, an accurate calculation of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ with the new function would imply an accurate calculation of the original experimental data.

An examination of the standard errors of fit among the two sets of regression analyses for the chloride and the sulphate anionic groups does not show divisions on the basis of the ion interaction parameters $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ (Tables 3.3 and 3.4). Thus, the same interpolation function can be used for all ion interaction parameters within a cation-anion pair. An examination of the error analyses next focuses upon whether there is any significant difference between the two anionic groups.

The standard errors of fit between values calculated with the published interpolation functions and the fourteen new interpolation equations for all ion pairs within the chloride anionic group are listed in Table 3.3. Generally, the lowest standard error of fit is obtained with the equations consisting of four interpolation coefficients (equations (34) to (38)). The fit with these functions is typically less than an order of magnitude better than the fit obtained with the equations containing three regression coefficients (equations (28) to (33)), and in many cases the improvement is less than 0.1 of an order of magnitude. However, the standard errors of fit among the proposed equations which contain two coefficients are typically one to two orders of magnitude higher than that for those containing three or four coefficients. Of the 26 ion interaction parameters that are regressed with the new functions, equation (35) produces the lowest standard errors of fit in 15 cases and the second best fit in 2 cases. The next best fits are obtained with equation (34), having the best fit and second best fit overall in 3 and 11 cases respectively, and equation (36), having the best fit overall in 4 cases and the second best fit in 3 cases. The accuracy obtained with equation (36) is not unexpected because some of the ion interaction

Table 3.3: continued.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
CaCl₂														
B ⁽⁰⁾	3.47×10^{-2}	2.36×10^{-2}	$.652 \times 10^{-2}$	$.572 \times 10^{-2}$	$.137 \times 10^{-2}$	$.262 \times 10^{-2}$	$.238 \times 10^{-2}$	$.196 \times 10^{-2}$	$.181 \times 10^{-2}$	$.391 \times 10^{-2}$	$.409 \times 10^{-3}$	$.317 \times 10^{-3}$	$.103 \times 10^{-2}$	$.725 \times 10^{-3}$
B ⁽¹⁾	$.128 \times 10^{-2}$	$.750 \times 10^{-2}$	$.180 \times 10^{-1}$	$.126 \times 10^{-1}$	$.147 \times 10^{-3}$	$.413 \times 10^{-3}$	$.293 \times 10^{-3}$	$.237 \times 10^{-2}$	$.165 \times 10^{-2}$	$.374 \times 10^{-2}$	$.438 \times 10^{-4}$	$.338 \times 10^{-4}$	$.571 \times 10^{-4}$	$.352 \times 10^{-3}$
C ⁺	$.365 \times 10^{-4}$	$.798 \times 10^{-4}$	$.103 \times 10^{-3}$	$.627 \times 10^{-4}$	$.420 \times 10^{-5}$	$.118 \times 10^{-4}$	$.837 \times 10^{-5}$	$.228 \times 10^{-4}$	$.150 \times 10^{-4}$	$.121 \times 10^{-4}$	$.125 \times 10^{-5}$	$.969 \times 10^{-6}$	$.163 \times 10^{-5}$	$.257 \times 10^{-5}$
MgCl₂														
B ⁽⁰⁾	$.442 \times 10^{-2}$	$.367 \times 10^{-2}$	$.622 \times 10^{-2}$	$.580 \times 10^{-2}$	$.134 \times 10^{-3}$	$.200 \times 10^{-2}$	$.162 \times 10^{-2}$	$.135 \times 10^{-2}$	$.100 \times 10^{-2}$	$.331 \times 10^{-2}$	$.401 \times 10^{-4}$	$.310 \times 10^{-4}$	$.524 \times 10^{-3}$	$.264 \times 10^{-3}$
B ⁽¹⁾	$.295 \times 10^{-1}$	$.314 \times 10^{-1}$	$.224 \times 10^{-1}$	$.243 \times 10^{-1}$	$.381 \times 10^{-2}$	$.159 \times 10^{-1}$	$.134 \times 10^{-1}$	$.139 \times 10^{-1}$	$.111 \times 10^{-1}$	$.194 \times 10^{-1}$	$.114 \times 10^{-2}$	$.880 \times 10^{-3}$	$.494 \times 10^{-2}$	$.344 \times 10^{-2}$
C ⁺	$.585 \times 10^{-4}$	$.128 \times 10^{-3}$	$.164 \times 10^{-3}$	$.101 \times 10^{-3}$	$.673 \times 10^{-5}$	$.189 \times 10^{-4}$	$.134 \times 10^{-4}$	$.370 \times 10^{-4}$	$.241 \times 10^{-4}$	$.194 \times 10^{-4}$	$.201 \times 10^{-5}$	$.155 \times 10^{-5}$	$.262 \times 10^{-5}$	$.413 \times 10^{-5}$
SrCl₂														
B ⁽⁰⁾	$.443 \times 10^{-2}$	$.461 \times 10^{-2}$	$.349 \times 10^{-2}$	$.379 \times 10^{-2}$	$.509 \times 10^{-3}$	$.143 \times 10^{-2}$	$.101 \times 10^{-2}$	$.107 \times 10^{-3}$	$.616 \times 10^{-3}$	$.214 \times 10^{-2}$	$.152 \times 10^{-3}$	$.117 \times 10^{-3}$	$.198 \times 10^{-3}$	$.333 \times 10^{-4}$
B ⁽¹⁾	$.920 \times 10^{-2}$	$.291 \times 10^{-2}$	$.445 \times 10^{-1}$	$.348 \times 10^{-1}$	$.106 \times 10^{-2}$	$.297 \times 10^{-2}$	$.211 \times 10^{-2}$	$.191 \times 10^{-2}$	$.168 \times 10^{-2}$	$.131 \times 10^{-1}$	$.316 \times 10^{-3}$	$.244 \times 10^{-3}$	$.411 \times 10^{-3}$	$.626 \times 10^{-3}$
C ⁺	$.390 \times 10^{-4}$	$.852 \times 10^{-4}$	$.110 \times 10^{-3}$	$.669 \times 10^{-4}$	$.448 \times 10^{-5}$	$.126 \times 10^{-4}$	$.894 \times 10^{-5}$	$.244 \times 10^{-4}$	$.160 \times 10^{-4}$	$.129 \times 10^{-4}$	$.134 \times 10^{-5}$	$.103 \times 10^{-5}$	$.174 \times 10^{-5}$	$.275 \times 10^{-5}$
BaCl₂														
B ⁽⁰⁾	$.192 \times 10^{-2}$	$.293 \times 10^{-2}$	$.517 \times 10^{-3}$	$.134 \times 10^{-3}$	$.411 \times 10^{-3}$	$.813 \times 10^{-4}$	$.140 \times 10^{-3}$	$.546 \times 10^{-4}$	$.144 \times 10^{-3}$	$.131 \times 10^{-3}$	$.120 \times 10^{-13}$	$.190 \times 10^{-8}$	$.173 \times 10^{-8}$	$.758 \times 10^{-9}$
B ⁽¹⁾	$.212 \times 10^{-1}$	$.105 \times 10^{-1}$	$.461 \times 10^{-1}$	$.402 \times 10^{-1}$	$.259 \times 10^{-2}$	$.108 \times 10^{-2}$	$.422 \times 10^{-3}$	$.132 \times 10^{-2}$	$.164 \times 10^{-2}$	$.554 \times 10^{-2}$	$.239 \times 10^{-12}$	$.120 \times 10^{-7}$	$.229 \times 10^{-7}$	$.183 \times 10^{-7}$
C ⁺	$.801 \times 10^{-3}$	$.125 \times 10^{-2}$	$.230 \times 10^{-3}$	$.965 \times 10^{-4}$	$.228 \times 10^{-3}$	$.879 \times 10^{-4}$	$.113 \times 10^{-3}$	$.765 \times 10^{-4}$	$.114 \times 10^{-3}$	$.109 \times 10^{-3}$	$.120 \times 10^{-13}$	$.105 \times 10^{-8}$	$.187 \times 10^{-8}$	$.106 \times 10^{-8}$

Table 3.4: Standard error of fit between published interpolation curves and interpolation equations in Table 3.2: sulphate anion group.

#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
Na₂SO₄													
B ⁽⁰⁾	.636x10 ⁻²	.887x10 ⁻²	.254x10 ⁻²	.721x10 ⁻³	.255x10 ⁻²	.898x10 ⁻³	.770x10 ⁻³	.102x10 ⁻²	.777x10 ⁻³	.762x10 ⁻³	.942x10 ⁻³	.675x10 ⁻³	.847x10 ⁻³
B ⁽¹⁾	.478x10 ⁻¹	.371x10 ⁻¹	.745x10 ⁻¹	.679x10 ⁻¹	.808x10 ⁻²	.257x10 ⁻¹	.220x10 ⁻¹	.182x10 ⁻¹	.153x10 ⁻¹	.405x10 ⁻¹	.686x10 ⁻²	.650x10 ⁻²	.125x10 ⁻¹
C [†]	.800x10 ⁻³	.122x10 ⁻²	.107x10 ⁻²	.682x10 ⁻³	.661x10 ⁻³	.395x10 ⁻³	.455x10 ⁻³	.291x10 ⁻³	.396x10 ⁻³	.598x10 ⁻³	.142x10 ⁻³	.959x10 ⁻⁴	.229x10 ⁻³
K₂SO₄													
B ⁽⁰⁾	.438x10 ⁻²	.396x10 ⁻²	.523x10 ⁻²	.507x10 ⁻²	.775x10 ⁻³	.117x10 ⁻²	.746x10 ⁻³	.617x10 ⁻³	.235x10 ⁻³	.232x10 ⁻²	.214x10 ⁻³	.161x10 ⁻³	.727x10 ⁻⁴
B ⁽¹⁾	.207x10 ⁻¹	.236x10 ⁻¹	.105x10 ⁻¹	.133x10 ⁻¹	.350x10 ⁻²	.557x10 ⁻²	.360x10 ⁻²	.455x10 ⁻²	.220x10 ⁻²	.755x10 ⁻²	.635x10 ⁻³	.393x10 ⁻³	.726x10 ⁻³
C [†]	.545x10 ⁻³	.119x10 ⁻²	.153x10 ⁻²	.936x10 ⁻³	.627x10 ⁻⁴	.176x10 ⁻³	.125x10 ⁻³	.341x10 ⁻³	.224x10 ⁻³	.180x10 ⁻³	.187x10 ⁻⁴	.145x10 ⁻⁴	.244x10 ⁻⁴
Li₂SO₄													
B ⁽⁰⁾	.790x10 ⁻³	.224x10 ⁻²	.379x10 ⁻²	.248x10 ⁻²	.908x10 ⁻⁴	.255x10 ⁻³	.181x10 ⁻³	.665x10 ⁻³	.447x10 ⁻³	.662x10 ⁻³	.271x10 ⁻⁴	.210x10 ⁻⁴	.338x10 ⁻⁴
B ⁽¹⁾	.769x10 ⁻¹	.459x10 ⁻¹	.161x10 ⁰	.139x10 ⁰	.502x10 ⁻²	.365x10 ⁻¹	.300x10 ⁻¹	.193x10 ⁻¹	.152x10 ⁻¹	.711x10 ⁻¹	.340x10 ⁻²	.314x10 ⁻²	.120x10 ⁻¹
C [†]	.162x10 ⁻³	.708x10 ⁻³	.158x10 ⁻²	.109x10 ⁻²	.521x10 ⁻⁴	.114x10 ⁻³	.101x10 ⁻³	.285x10 ⁻³	.218x10 ⁻³	.254x10 ⁻³	.955x10 ⁻⁵	.131x10 ⁻⁴	.184x10 ⁻⁴
CaSO₄													
B ⁽⁰⁾	.356x10 ⁻²	.574x10 ⁻²	.772x10 ⁻²	.537x10 ⁻²	.279x10 ⁻²	.361x10 ⁻²	.347x10 ⁻²	.434x10 ⁻²	.391x10 ⁻²	.193x10 ⁻²	.878x10 ⁻³	.106x10 ⁻²	.115x10 ⁻³
B ⁽¹⁾	.657x10 ⁻¹	.468x10 ⁻¹	.177x10 ⁰	.145x10 ⁰	.506x10 ⁻¹	.276x10 ⁻¹	.332x10 ⁻¹	.458x10 ⁻¹	.477x10 ⁻¹	.162x10 ⁻¹	.107x10 ⁻¹	.131x10 ⁻¹	.856x10 ⁻²
C [†]	.383x10 ⁻⁴	.837x10 ⁻⁴	.108x10 ⁻³	.657x10 ⁻⁴	.440x10 ⁻⁵	.124x10 ⁻⁴	.878x10 ⁻⁵	.239x10 ⁻⁴	.158x10 ⁻⁴	.127x10 ⁻⁴	.131x10 ⁻⁵	.102x10 ⁻⁵	.171x10 ⁻⁵
MgSO₄													
B ⁽⁰⁾	.841x10 ⁻²	.581x10 ⁻²	.153x10 ⁻¹	.135x10 ⁻¹	.174x10 ⁻²	.483x10 ⁻²	.420x10 ⁻²	.329x10 ⁻²	.286x10 ⁻²	.789x10 ⁻²	.134x10 ⁻²	.125x10 ⁻²	.241x10 ⁻²
B ⁽¹⁾	.499x10 ⁻¹	.248x10 ⁻¹	.122x10 ⁰	.103x10 ⁰	.574x10 ⁻²	.161x10 ⁻¹	.115x10 ⁻¹	.323x10 ⁻²	.123x10 ⁻²	.435x10 ⁻¹	.172x10 ⁻²	.123x10 ⁻²	.223x10 ⁻²
B ⁽²⁾	.344x10 ⁺¹	.571x10 ⁰	.152x10 ⁺²	.120x10 ⁺²	.674x10 ⁰	.153x10 ⁺¹	.122x10 ⁺¹	.129x10 ⁰	.723x10 ⁻¹	.494x10 ⁺¹	.201x10 ⁻¹	.156x10 ⁻¹	.389x10 ⁰
C [†]	.609x10 ⁻³	.493x10 ⁻³	.896x10 ⁻³	.825x10 ⁻³	.268x10 ⁻³	.466x10 ⁻³	.429x10 ⁻³	.384x10 ⁻³	.354x10 ⁻³	.620x10 ⁻³	.171x10 ⁻³	.155x10 ⁻³	.271x10 ⁻³

parameters for NaCl, KCl and HCl are regressed to high temperatures with a published function which is the same as equation (36). The standard errors of fit of $B^{(0)}$ and $B^{(1)}$ for LiCl, $B^{(1)}$ for NaCl and $B^{(0)}$, $B^{(1)}$ and C^Φ for $BaCl_2$ exceed the accuracy of the ion interaction parameters obtained with the original function. Hence, several of the proposed interpolation functions, including equation (35), are equally accurate for predicting these six ion interaction parameters. The extremely low standard error of fit results from recalculating values obtained from functions with two or three terms with equations having containing three, four or five terms, or in the case of $BaCl_2$, due to fitting a limited number of data points with a regression function containing five terms. Of the 6 remaining cases, the difference between the standard errors of fit obtained from equation (35) and the best function is always less than an order of magnitude.

Overall, the single function which best represents the values of all cation-anion interaction parameters from 0°C to 200°C for the chloride anionic group is:

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^3 - T_R^3] + d[\ln T - \ln T_R] \quad (35)$$

where: T and T_R are in temperature units of °C

The standard errors of fit for the 14 ion interaction parameters within the sulphate anionic group (Table 3.4) show a pattern which is very similar to the chloride group. Again the lowest standard errors of fit between the values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^Φ calculated with the published interpolation functions and the fourteen proposed equations are generally calculated by the interpolation equations that have four interpolation coefficients. As with the chloride anionic group, equation (35) produces the best results, having the best overall fit in 10 cases and second best fit in 3 of 16 cases. The difference between the standard errors of fit calculated with equation (35) and the function which best represents the published data is less than an order of magnitude in the 3 remaining cases.

Considering both anionic groups together, equation (35) is the best of the fourteen proposed equations for reproducing all the ion interaction parameters from 0°C to 200°C. This function or a simplified form of it (i.e. the "b" and "c" constants equal 0) produces the lowest standard errors of fit between values calculated using published interpolation functions and the proposed functions in 25 cases and the second best fit in 5 cases. Also, in another 3 cases the standard errors of fit of equation (35) exceed the accuracy of the original data which was regressed. Thus, equation (35) or a simplified form of it, best represents values obtained from the published sources in 28 of 42 cases. The difference between the standard errors of fit from equation (35) and the functions which best fit the data in the 9 remaining cases in which equation (35) does not produce the best or second best fit is always less than an order of magnitude. The calculated interpolation coefficients for equation (35), along with the values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ at 25°C for the fourteen cation-anion pairs that were re-regressed are listed in Table 3.5. Because the published interpolation functions for $\beta^{(1)}$ of NaCl (Silvester and Pitzer, 1977) and $\beta^{(0)}$ and $\beta^{(1)}$ of LiCl (Holmes and Mesmer, 1983a) are exactly the same as equation (24), the interpolation coefficients calculated for equation (24) are selected rather than those for equation (35). In order to show the accuracy of calculations using the new interpolation functions versus those from the published sources, Figures 3 and 4 contain plots of the values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ for the two anionic groups.

A Model for Estimating Missing Ion Interaction Parameters

This section presents a technique for providing high temperature values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ when only the values of these ion interaction parameters at 25°C are known. The basis for this interpolation model comes from the analyses of the trends of these parameters and the new interpolation function (equation (35)).

An examination of published data for the chloride group shows three prominent trends. First, the values of $\beta^{(0)}$ and $\beta^{(1)}$ at 25°C are divided into two groups on the basis of

Table 3.5: Coefficients for the new interpolation function (equation (35)) for calculating $g^{(0)}$, $g^{(1)}$, $g^{(2)}$ and C^* from 0 to 200°C for the previously published regression equations.

	$Y(T)$	$Y(T_R)$	a	b	c	d
LiCl	$g^{(0)}$	0.14847×10^0	-0.15463×10^{-3}	0.79515×10^{-11}	0.0	0.0
	$g^{(1)}$	0.30700×10^0	0.63604×10^{-3}	-0.20272×10^{-9}	0.0	0.0
	C^*	0.37100×10^{-2}	-0.54202×10^{-4}	0.13922×10^{-6}	-0.19939×10^{-9}	-0.58357×10^{-5}
NaCl	$g^{(0)}$	0.76500×10^{-1}	0.90108×10^{-3}	-0.57289×10^{-5}	0.10557×10^{-7}	0.53818×10^{-3}
	$g^{(1)}$	0.26640×10^0	0.64702×10^{-3}	0.10713×10^{-5}	0.0	0.0
	C^*	0.12700×10^{-2}	-0.13002×10^{-3}	0.63943×10^{-6}	-0.10437×10^{-8}	-0.35192×10^{-4}
KCl	$g^{(0)}$	0.48080×10^{-1}	0.70143×10^{-3}	-0.42327×10^{-5}	0.82284×10^{-8}	0.48318×10^{-3}
	$g^{(1)}$	0.21875×10^0	0.12009×10^{-2}	-0.12262×10^{-5}	0.36271×10^{-8}	0.26620×10^{-2}
	C^*	-0.78800×10^{-3}	-0.74399×10^{-4}	0.44194×10^{-6}	-0.86816×10^{-9}	-0.55653×10^{-4}
CsCl	$g^{(0)}$	0.33520×10^{-1}	0.82182×10^{-3}	-0.52680×10^{-5}	0.11424×10^{-7}	0.76925×10^{-3}
	$g^{(1)}$	0.42900×10^{-1}	0.18041×10^{-2}	-0.14087×10^{-5}	0.20278×10^{-8}	0.35167×10^{-3}
	C^*	-0.26200×10^{-3}	-0.69008×10^{-4}	0.44147×10^{-6}	-0.92257×10^{-9}	-0.91678×10^{-4}
HCl	$g^{(0)}$	0.17416×10^0	0.19074×10^{-1}	-0.24649×10^{-3}	0.88845×10^{-6}	-0.42955×10^{-1}
	$g^{(1)}$	0.28799×10^0	0.21784×10^{-3}	0.88333×10^{-5}	-0.70143×10^{-8}	0.27283×10^{-3}
	C^*	0.0	---	---	---	---
MgCl ₂	$g^{(0)}$	0.35093×10^0	0.32321×10^{-3}	-0.68498×10^{-5}	0.25418×10^{-7}	-0.16178×10^{-3}
	$g^{(1)}$	0.16508×10^{-1}	-0.76391×10^{-3}	0.58968×10^{-4}	-0.16970×10^{-6}	0.45708×10^{-2}
	C^*	0.23010×10^{-2}	-0.86988×10^{-4}	0.24120×10^{-6}	-0.34070×10^{-9}	0.16519×10^{-4}
CaCl ₂	$g^{(0)}$	0.30534×10^0	-0.67362×10^{-3}	0.47264×10^{-5}	-0.20320×10^{-7}	0.19049×10^{-2}
	$g^{(1)}$	0.17083×10^{-1}	0.29703×10^{-2}	0.13518×10^{-4}	-0.63690×10^{-8}	-0.18251×10^{-2}
	C^*	0.76120×10^{-3}	-0.53341×10^{-4}	0.14544×10^{-6}	-0.20188×10^{-9}	-0.11969×10^{-4}
SrCl ₂	$g^{(0)}$	0.28344×10^0	0.69640×10^{-3}	-0.83431×10^{-5}	0.24810×10^{-7}	0.75072×10^{-3}
	$g^{(1)}$	0.16256×10^{-1}	0.31752×10^{-2}	0.49051×10^{-5}	0.52761×10^{-7}	-0.97344×10^{-3}
	C^*	-0.31500×10^{-2}	-0.57620×10^{-4}	0.15896×10^{-6}	-0.22336×10^{-9}	0.37020×10^{-5}
BaCl ₂	$g^{(0)}$	0.26280×10^0	0.89444×10^{-3}	-0.75336×10^{-5}	0.13655×10^{-7}	-0.13516×10^{-3}
	$g^{(1)}$	0.14983×10^{-1}	0.71761×10^{-2}	-0.34170×10^{-4}	0.18132×10^{-6}	-0.11183×10^{-1}
	C^*	-0.19378×10^{-1}	-0.25440×10^{-3}	0.16908×10^{-5}	-0.31178×10^{-8}	-0.51529×10^{-3}
Li ₂ SO ₄	$g^{(0)}$	0.13082×10^0	0.63915×10^{-3}	-0.41291×10^{-5}	0.44347×10^{-8}	0.12790×10^{-3}
	$g^{(1)}$	0.12913×10^{-1}	0.58838×10^{-2}	-0.85246×10^{-4}	0.44014×10^{-6}	-0.13068×10^{-2}
	C^*	-0.25280×10^{-2}	-0.34280×10^{-3}	0.15000×10^{-5}	-0.12871×10^{-8}	0.83980×10^{-3}

Table 3.5: continued.

	Y(T)	Y(T _R)	a	b	c	d
Na ₂ SO ₄	B ⁽⁰⁾	0.18110x10 ⁻¹	0.25725x10 ⁻²	-0.15171x10 ⁻⁴	0.32307x10 ⁻⁷	0.31322x10 ⁻²
	B ⁽¹⁾	0.10559x10 ⁺¹	0.84964x10 ⁻²	-0.66674x10 ⁻⁴	0.26858x10 ⁻⁶	0.45448x10 ⁻²
	C ⁺	0.57030x10 ⁻²	-0.39745x10 ⁻³	0.17116x10 ⁻⁵	-0.24303x10 ⁻⁸	-0.11450x10 ⁻²
K ₂ SO ₄	B ⁽⁰⁾	0.0	0.14510x10 ⁻²	-0.69712x10 ⁻⁵	0.24159x10 ⁻⁷	0.11649x10 ⁻²
	B ⁽¹⁾	0.11023x10 ⁺¹	0.80167x10 ⁻²	-0.39371x10 ⁻⁴	0.10856x10 ⁻⁶	0.18137x10 ⁻¹
	C ⁺	0.18811x10 ⁻¹	0.10324x10 ⁻³	-0.22638x10 ⁻⁵	0.32108x10 ⁻⁸	-0.23041x10 ⁻³
Cs ₂ SO ₄	B ⁽⁰⁾	0.80350x10 ⁻¹	0.30808x10 ⁻²	-0.10147x10 ⁻⁴	0.15523x10 ⁻⁷	-0.23765x10 ⁻²
	B ⁽¹⁾	0.13660x10 ⁺¹	-0.57148x10 ⁻²	-0.52831x10 ⁻⁵	0.24778x10 ⁻⁶	0.35880x10 ⁻¹
	C ⁺	-0.24731x10 ⁻²	-0.56187x10 ⁻⁴	0.15392x10 ⁻⁶	-0.21473x10 ⁻⁹	-0.62782x10 ⁻⁵
MgSO ₄	B ⁽⁰⁾	0.21499x10 ⁰	0.12004x10 ⁻²	-0.10826x10 ⁻⁴	0.48239x10 ⁻⁷	-0.17922x10 ⁻²
	B ⁽¹⁾	0.33646x10 ⁺¹	0.12505x10 ⁻¹	-0.49188x10 ⁻⁴	0.29291x10 ⁻⁶	-0.18739x10 ⁻¹
	B ⁽²⁾	-0.32743x10 ⁺²	-0.14116x10 ⁰	-0.10316x10 ⁻²	-0.19748x10 ⁻⁴	0.94485x10 ⁻¹
	C ⁺	0.69930x10 ⁻²	-0.13941x10 ⁻³	0.80675x10 ⁻⁶	-0.32224x10 ⁻⁸	0.30977x10 ⁻⁴
NaOH	B ⁽⁰⁾	0.91889x10 ⁻¹	0.85391x10 ⁻³	-0.10023x10 ⁻⁴	0.26696x10 ⁻⁷	-0.75941x10 ⁻³
	B ⁽¹⁾	0.25302x10 ⁰	0.13036x10 ⁻²	0.70706x10 ⁻⁵	-0.22250x10 ⁻⁷	0.38312x10 ⁻²
	C ⁺	0.36100x10 ⁻²	-0.13484x10 ⁻³	0.86211x10 ⁻⁶	-0.19111x10 ⁻⁸	0.26884x10 ⁻⁴

their cation valence, with the group comprised of cations with a charge of +1 having significantly lower values than the group comprised of cations with a charge of +2 (Figure 5). This pattern typically continues to 200°C. The C^ϕ values do not exhibit any dependency on ionic radius of the cation. The second pattern, also evident at a temperature of 25°C, is that the values of the ion interaction parameters follow a consistent trend; that is as the ionic radius of the cation increases, the corresponding values of $B^{(0)}$, $B^{(1)}$ and C^ϕ decrease (Figure 5). This pattern is not unexpected because the mean activity coefficients of the electrolytes follow a trend based on the ionic radius of the cation. The trend is reversed with $\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl} > \gamma_{CsCl}$ (Baes and Mesmer, 1976). However, $B^{(1)}$ of $MgCl_2$ and C^ϕ of $CsCl$ are slightly below and above their respective expected positions. Holmes and Mesmer (1983a) also noted this pattern among the values of $B^{(0)}$ and $B^{(1)}$ of the $LiCl$, $NaCl$, KCl and $CsCl$ ion pairs. The third pattern shown by Figure 1 is that the curves for all ion pairs, grouped by ion interaction parameter and by the charge of the cation, have a similar shape between 0°C and 200°C. For example, within the chloride ion group the curves of $B^{(0)}$ for univalent cations are generally convex with values of $B^{(0)}$ at 25°C not much different than $B^{(0)}$ at higher temperatures. The curves of $B^{(0)}$ for divalent cations are generally convex, but the curves turn up near 175°C for $MgCl_2$ and $SrCl_2$. The curves of $B^{(1)}$ for divalent cations are all generally concave and the plot of the univalent cations is essentially linear upwards. The values of C^ϕ , for both cation charges are concave with the values at 25°C greater than those at higher temperatures. Holmes and Mesmer (1983a) noted that the change in the values of $B^{(0)}$ and $B^{(1)}$ among ion pairs $LiCl$, $NaCl$, KCl and $CsCl$ corresponded to a change in the ionic radius of the cations, not only at 25°C, but at temperatures up to 200°C as well.

Although not as much data are available for the sulphate anionic group, some of the same patterns exhibited by the chloride group are observed. First, the values of $B^{(0)}$ and $B^{(1)}$ at 25°C, as shown by Figure 5, can be divided into two groups on the basis of the charge of the cation member of the cation-anion pair and again this pattern is not present among the

C° data. Both the $\beta^{(0)}$ and $\beta^{(1)}$ values of the ion pair containing a divalent cation have greater values than those ion pairs containing a univalent cation. Values of the ion interaction parameters at 25°C for CaSO_4 , BeSO_4 , SrSO_4 and Rb_2SO_4 are plotted on Figure 5, even though high temperature data do not exist for these ion pairs, in order to verify the grouping of values according to the charge of the cation. The trend again generally continues to high temperatures. Second, the values of $\beta^{(0)}$, $\beta^{(1)}$ and $\beta^{(2)}$ at 25°C show a consistent trend when plotted against the ionic radius of the cation (Figure 5). However, the pattern varies among the ion interaction parameters. For example, the plots of both $\beta^{(0)}$ and $\beta^{(1)}$ for univalent cations are concave, $\beta^{(0)}$ and $\beta^{(2)}$ for divalent cations are concave but decrease as the ionic radius of the cation increases; and $\beta^{(1)}$ for divalent cations are convex with a maxima near the MgSO_4 . Unlike the chloride group, the values of C° do not exhibit a trend. Third, the overall shape of the plots of the high temperature values do not show any particular pattern for either $\beta^{(0)}$ or C° and there are insufficient data for an accurate discussion of the $\beta^{(2)}$ curves. The only pattern that appears is an increasing values of $\beta^{(1)}$ with an increasing temperature. Because the C° term is only significant at high molalities, it is treated as an arbitrary fitting parameter and thus may not show any pattern (Holmes and Mesmer, 1983a).

The patterns exhibited by the values of $\beta^{(0)}$ and $\beta^{(1)}$ at 25°C for the chloride anionic group versus the ionic radius of the cation are repeated by other halogens. As illustrated by Figure 6, the values of $\beta^{(0)}$ and $\beta^{(1)}$ for both iodide and bromide decreases in a concave and a convex manner, respectively, as the cation radius increases. Also, the values of $\beta^{(0)}$ and $\beta^{(1)}$ for the divalent cations are consistently greater than those for univalent cations, and secondly, these values increase as the ionic radius of the halogen increase. As in the case of chloride and sulphate, there is not a not a consistent trend. These latest trends confirm that the values of $\beta^{(0)}$ and $\beta^{(1)}$ follow consistent trends, and thus values of $\beta^{(0)}$ and $\beta^{(1)}$ can be estimated if they have not been determined from experimental data.

VERIFICATION OF THE ION INTERACTION PARAMETER MODEL

Because of the trends exhibited by the known values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^* , it should be possible to estimate the values of these ion interaction parameters for similar ion pairs at 25°C, as well as at higher temperatures. In order to test how well equation (35), used in conjunction with the observed trends, can be used to determine missing values at both 25°C and higher temperatures, ion interaction parameters for RbCl and SrSO_4 , and the solubility of celestite to 90°C in NaCl solutions will be estimated and compared to published data in this section. A list of all interpolating coefficients, both re-calculated from published sources and estimated here, are listed in Appendix 1.

The values of $\beta^{(0)}$, $\beta^{(1)}$ and C^* for RbCl are reported at 25°C by Pitzer and Mayorga (1973), and by Rand (1984). Extrapolations of $\beta^{(0)}$ and $\beta^{(1)}$ to temperatures not far above 25°C can be calculated with the temperature derivatives from Silvester and Pitzer (1978). Published values of these ion interaction parameters at 25°C and values extrapolated to 50°C from the 25°C values from Pitzer and Mayorga (1973) are listed in Table 3.6.

Based upon the ionic radius of Rb^+ , the values of $\beta^{(0)}$, $\beta^{(1)}$ and C^* at 25°C for the RbCl ion pair from Pitzer and Mayorga (1973) and Rand (1984) lie, as predicted from Figure 5, between the corresponding values for KCl and CsCl. If it is assumed that the values of these parameters to 200°C follow the same trend exhibited by KCl and CsCl, then the interpolation function for RbCl could be represented by equation (35). Interpolation constants from the KCl or CsCl interpolation function and a 25°C intercept of the value given by Pitzer and Mayorga (1973) are used in conjunction with equation (35). Estimates of the values of $\beta^{(0)}$, $\beta^{(1)}$ and C^* to 200°C for RbCl are calculated with the interpolation constant for CsCl (Table 3.7). The values of $\beta^{(0)}$ and $\beta^{(1)}$ at 50°C calculated with equation (35) compare very well with the values calculated with the temperature derivatives of Silvester and Pitzer (1978), differing only by 1.0% and 2.5%, respectively.

The primary validation of the model presented here focuses upon the prediction of high temperature values of the Pitzer equation parameters for SrSO_4 . Reardon and

Table 3.6: Published ion interaction parameters for RbCl.

temperature	$\beta^{(0)}$	$\beta^{(1)}$	C°	maximum molality	notes
25°C	0.0441	0.1483	-0.00101	5.0	1
25°C	0.04319	0.15398	-0.001098	7.8	2
50°C	0.0579	0.1860	-----	0.8	3

1: from Pitzer and Mayorga (1973).

2: from Rard (1984).

3: calculated with temperature derivatives from Silvester and Pitzer (1978).

Table 3.7: Values of $\beta^{(0)}$, $\beta^{(1)}$ and C^* for RbCl estimated with the new interpolation model.

temperature	$\beta^{(0)}$	$\beta^{(1)}$	C^*
0°C	0.020658	0.10682	0.0011703
25°C	0.044100	0.14830	-0.0010100
50°C	0.056551	0.19074	-0.0020719
75°C	0.064337	0.23190	-0.0027286
100°C	0.068661	0.27191	-0.0030821
125°C	0.070634	0.31094	-0.0032238
150°C	0.071346	0.34918	-0.0032424
175°C	0.071877	0.38681	-0.0032255
200°C	0.073304	0.42401	-0.0032603

interpolation coefficients ¹ :	a	b	c	d
$\beta^{(0)}$	0.82182×10^{-3}	-0.52680×10^{-5}	0.11424×10^{-7}	0.76925×10^{-3}
$\beta^{(1)}$	0.18041×10^{-2}	-0.14087×10^{-5}	0.20278×10^{-8}	-0.35167×10^{-3}
C^*	-0.69008×10^{-4}	0.44147×10^{-6}	-0.92257×10^{-9}	-0.91678×10^{-4}

1: estimated RbCl coefficients, from CsCl.

Armstrong (1987) present expressions for determining values of the ion interaction parameters for SrSO_4 to 90°C . These expressions are based on celestite ($\text{SrSO}_{4(s)}$) solubility (Table 3.8) and use the $\beta^{(0)}$ and $\beta^{(1)}$ values of CaSO_4 from Harvie et al. (1984) as estimates for SrSO_4 at 25°C .

New estimates of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ for SrSO_4 at 25°C are based on the relationship of the ionic radius of Sr^+ to that of the other cations. Because Sr^+ has a charge of +2 and its ionic radius is greater than that of Mg^{+2} , estimates of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ were estimated from Figure 5 and are 0.2, 3.0, -50.0 and 0.005, respectively (Table 3.9). These values are quite similar to the values used by Reardon and Armstrong (1987). Assuming that the high temperature values of the ion interaction parameters for SrSO_4 can be represented by equation (35), and that the curves should be similar to those of MgSO_4 , then estimates of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ to 200°C can be obtained.

The solubility of celestite in NaCl solutions, with the molality of NaCl ranging from 0.1 to 5.0, is calculated at 25°C and 90°C . Celestite solubility calculations obtained using the present model are compared to estimates obtained using the ion interaction parameters determined by Reardon and Armstrong (1987). The values of the equilibrium constant for the dissociation reaction of celestite are from Reardon and Armstrong (1987). The replication of results is very good (Figure 7). However, because the molality of SrSO_4 in these solutions is very small compared to the molality of NaCl, the system will not be very sensitive to the ion interaction parameters for SrSO_4 . As an additional check on the applicability of the new model, the mean activity coefficients of SrSO_4 in NaCl solutions with the ionic strength of the solution ranging from 0.001 to 10.0, at both 25°C and 90°C , are calculated using the two sets of ion interaction parameters. The estimates obtained with the new model, while slightly higher than those obtained using the data of Reardon and Armstrong (1987), are good (Figure 8). The fit between the two sets of data is especially good in the region of high ionic strengths (0.1 to 10.0), where the Pitzer model is most appropriate. Another test involves combining Reardon and Armstrong's (1987) data at

Table 3.8: Published ion interaction parameters for SrSO_4

temperature	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C	maximum molality	notes
25°C	0.2000	3.1973	-78.00	0.0	5.0	1
50°C	0.2000	4.5623	-101.00	0.0	5.0	2
90°C	0.2000	6.7463	-137.80	0.0	5.0	2

1: from Reardon and Armstrong (1987).

2: calculated with temperature derivatives from Reardon and Armstrong (1987).

Table 3.9: Values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $C^\ddagger$ for SrSO_4 estimated with the new interpolation model.

temperature	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\ddagger$
25°C	0.20	3.00	-60.00	-0.005
90°C ¹	0.2302	3.6250	-90.903	-0.01105
90°C ²	0.2302	3.8226	-108.90	0.0

interpolation coefficients ³ :	a	b	c	d
$\beta^{(0)}$	0.12004×10^{-2}	-0.10826×10^{-4}	0.48239×10^{-7}	-0.17922×10^{-2}
$\beta^{(1)}$	0.12505×10^{-1}	-0.49188×10^{-4}	0.29291×10^{-6}	-0.18739×10^{-1}
$\beta^{(2)}$	-0.14116×10^0	-0.10316×10^{-2}	-0.19748×10^{-4}	0.94485×10^{-1}
$C^\ddagger$	-0.13941×10^{-3}	0.80675×10^{-6}	-0.32224×10^{-8}	0.30977×10^{-4}

1: calculated with our estimates at 25°C and the new interpolation function.

2: calculated with Reardon and Armstrong's (1987) data at 25°C and equation (35).

3: estimated SrSO_4 coefficients from MgSO_4 .

25°C with the temperature extrapolation model of equation (35) to calculate mean activity coefficients at 90°C. The results of these calculations, illustrated by Figure 8, show that the activity coefficients obtained by combining the data of Reardon and Armstrong (1987) at 25°C and the new interpolation model match the values obtained by using both Reardon and Armstrong's (1987) high temperature data. This latter simulation produces a slightly better fit over the entire range of ionic strength than when both the new estimates at 25°C and the equation (35) are combined.

These tests indicate that the proposed model for predicting ion interaction parameters can be successful for estimating missing ion interaction parameters at high temperatures. Greater accuracy is obtained when values of the ion interaction parameters are previously known at 25°C and are used as a starting point for the high temperature extrapolations with equation (35). The best set of ion interaction parameters at 25°C for mineral solubility studies in brines is provided by Harvie et al. (1984). Other sources of data for the Pitzer equation model that were determined through mineral solubility experiments include Monnin and Schott (1984), Reardon and Armstrong (1987) and Reardon and Beckie (1987). Combining their values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ at 25°C with equation (35) and interpolation coefficients for equation (35) from similar ion pairs, will provide a reasonable data base for estimating the solubilities of many minerals to high temperatures.

The third application of the model is designed to show that estimates of not only the values of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ for BeCl_2 from 0°C to 200°C can be obtained, but also that the model can estimate the values of the ion interaction parameters at 25°C. In contrast to the two preceding studies in which ion interaction parameters for RbCl and SrSO_4 are known at both 25°C and higher temperatures, these data are not available for BeCl_2 . The ionic radius of Be^{+2} at 25°C is less than the ionic radius of Mg^{+2} , thus the values of the ion interaction parameters for BeCl_2 should plot above those MgCl_2 (Figure 5). Following the trends exhibited by Figure 5, the estimated values of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ for BeCl_2 at 25°C are

0.375, 1.70 and 0.01, respectively. Next, if it can be assumed that the trends to 200°C shown by the chloride ion pairs with a cation charge of +2 (Figure 1) are the same for BeCl_2 , then equation (35) can be used as the high temperature interpolation function and the interpolation coefficients for MgSO_4 can be used. Estimates of the ion interaction parameters to 200°C obtained through this method are listed in Table 3.10.

CONCLUSIONS

The Pitzer equation approach to the calculation of activity coefficients has greatly enhanced the validity of predictions of mineral solubility in brines. However, there are two limitations with the application of the Pitzer equations at high temperatures. The first, and the main, limitation of this technique is the lack of ion interaction parameters ($B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ) for calculations at temperatures well above 25°C, and below 25°C. Secondly, while a few interpolation equations used to estimate ion interaction parameters at high temperatures are available for a limited number of major ion pairs, the consistency of the mathematical form of these expressions impedes them from being efficiently incorporated into geochemical codes.

Techniques have been presented here which will reduce these problems. First, existing interpolation functions have been standardized into a single equation that will predict values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ over the temperature range of 0°C to 200°C. Second, a model for predicting the values of these ion interaction parameters at both 25°C and higher temperatures, based upon observed trends of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ , has been proposed. This research has focused upon certain important elements in natural waters, the alkali elements (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the alkali earth elements (Be^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2}) paired with either Cl^- or SO_4^{2-} .

Specific conclusions drawn from this study are:

1. Published interpolation functions for predicting values of $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^ϕ at temperatures above 25°C have been successfully refit to a single interpolation

Table 3.10: Values of $B^{(0)}$, $B^{(1)}$ and C^Φ for BeCl_2 estimated with the new interpolation model.

temperature	$B^{(0)}$	$B^{(1)}$	C^Φ	
0°C	0.37207	1.6491	0.0118990	
25°C	0.37500	1.7000	0.0100000	
50°C	0.37290	1.7761	0.0082517	
75°C	0.36706	1.8927	0.0067363	
100°C	0.35982	2.0348	0.0054247	
125°C	0.35356	2.1867	0.0042857	
150°C	0.35066	2.3325	0.0032878	
175°C	0.35350	2.4565	0.0023993	
200°C	0.36446	2.5427	0.0015884	

interpolation coefficients ¹ :	a	b	c	d
$B^{(0)}$	0.32321×10^{-3}	-0.68498×10^{-5}	0.25418×10^{-7}	-0.16178×10^{-3}
$B^{(1)}$	-0.76391×10^{-3}	0.58968×10^{-4}	-0.16970×10^{-6}	0.45708×10^{-2}
C^Φ	-0.86988×10^{-4}	0.24120×10^{-6}	-0.34070×10^{-9}	0.16519×10^{-4}

1: estimated BeCl_2 coefficients, from MgCl_2 .

function, valid from 0°C to 200°C. This single interpolation equation can be readily programmed into existing geochemical codes and utilizes a data base of interpolation coefficients which is both concise and consistent. The new interpolation equation is:

$$Y(T) = Y(T_R) + a[T - T_R] + b[T^2 - T_R^2] + c[T^3 - T_R^3] + d[\ln T - \ln T_R] -$$

2. A plot of the values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ at 25°C versus the ionic radius of the cation member of the ion pair reveals two important trends. First, the values of $\beta^{(0)}$ and $\beta^{(1)}$ for both the chloride and sulphate anionic groups plot as distinct regions based on the charge of the cation, with values of the ion interaction parameter within each group increasing as the charge of the cation increases. This trend is not present among the C^ϕ values. Secondly, both anion groups show that as the ionic radius of the cation increases, the value of the ion interaction parameter typically decreases. Thus, unknown values of the Pitzer equation parameters at 25°C for a specific ion pair can be approximated given the ionic radius of the cation, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^ϕ values for an ion pair within the same anionic group, the same cation charge and a cation with a similar ionic radius.
3. Plots of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ for the chloride anionic group and $\beta^{(1)}$ of the sulphate anionic group follow distinct trends from 0°C to 200°C based upon the anionic group, the ion interaction parameter, and the charge of the cation member of the ion pair. Thus, ion interaction parameters at high temperatures and temperatures to 0°C can be approximated by using the new interpolation function, substituting the interpolation coefficient for a similar ion pair and using the known value of the parameter at 25°C as a starting point for the extrapolation.

4. Based upon the limited verification of the model undertaken here (activity coefficients of RbCl and SrSO₄, and the solubility of celestite), the application of the proposed model for estimating ion interaction parameters from 0°C to 200°C from known values at 25°C, and to estimate values at 25°C when no data exists, appears valid. However, more tests are required to fully verify the model. These tests should focus upon mineral solubility experiments. Presently, the best combination of data for studying mineral solubility in brines with fluid temperatures to 200°C, is to combine the existing ion interaction parameters based upon mineral solubility studies at 25°C (Harvie et al., 1984, Monnin and Schott, 1984, Reardon and Armstrong, 1987, Reardon and Beckie, 1987) with the new interpolation equation, and use interpolation coefficients from similar cation-anion pairs.

The interpolation functions proposed in this study for the major cation-anion pairs found in most natural waters are suitable for most geological studies. Interpolation equations for most minor elements have not been sufficiently verified with mineral solubility experiments. Typically these trace elements present in concentrations several orders of magnitude less than the major species (e.g. Ba⁺² in a NaCl subsurface brine). Because the ion interaction parameters of the major species dominate the mineral solubility calculations, mineral solubilities are not very sensitive to the ion interaction parameters of the trace elements and the model proposed here is suitable.

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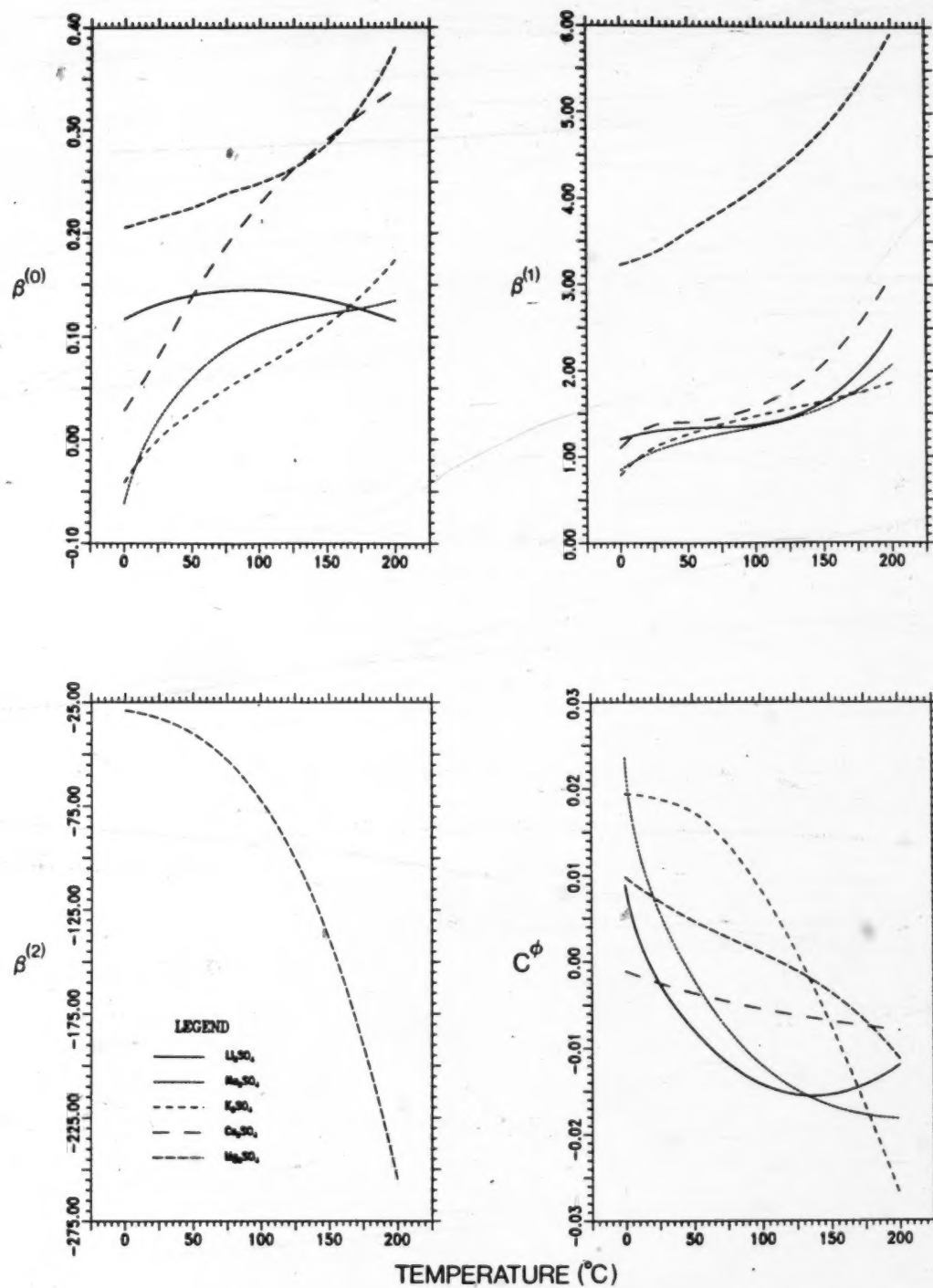


Figure 2. Published values of the cation-anion interaction parameters as a function of temperature for the sulphate anionic group.

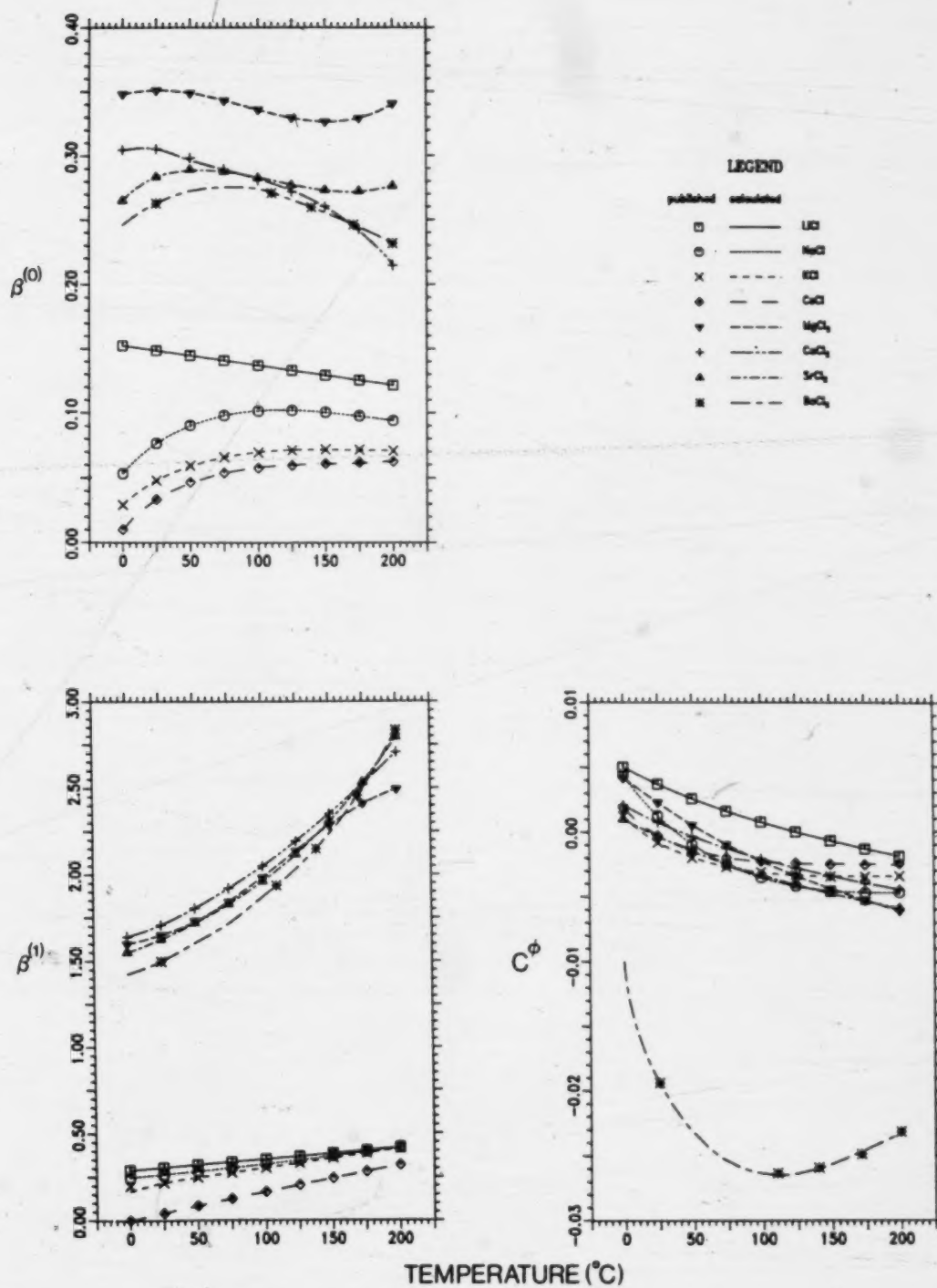


Figure 3.

Comparison of the cation-anion interaction parameters from published sources and equation (35) as a function of temperature, for the chloride anionic group.

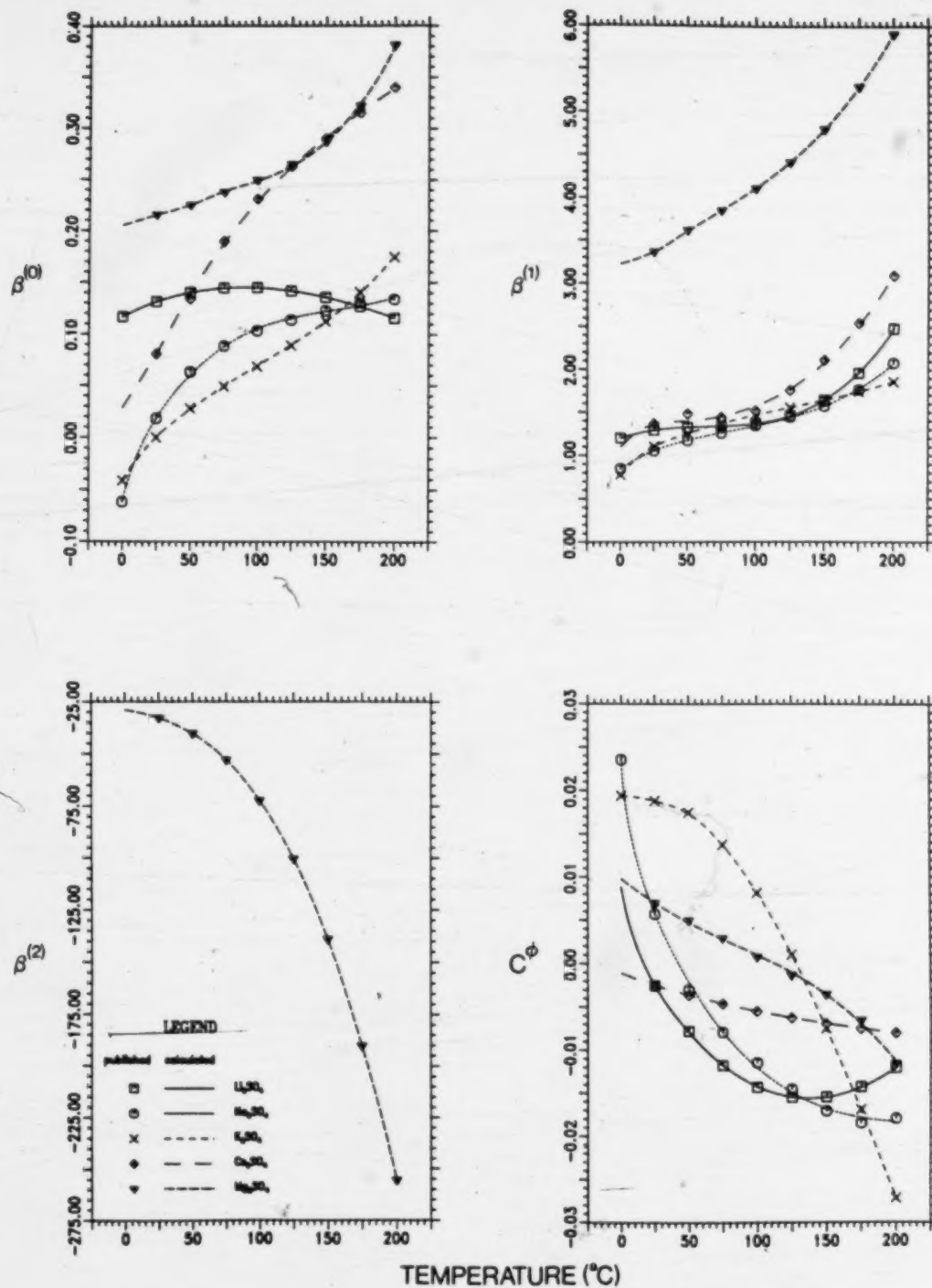


Figure 4.

Comparison of the cation-anion interaction parameters from published sources and equation (35) as a function of temperature, for the sulphate anionic group.

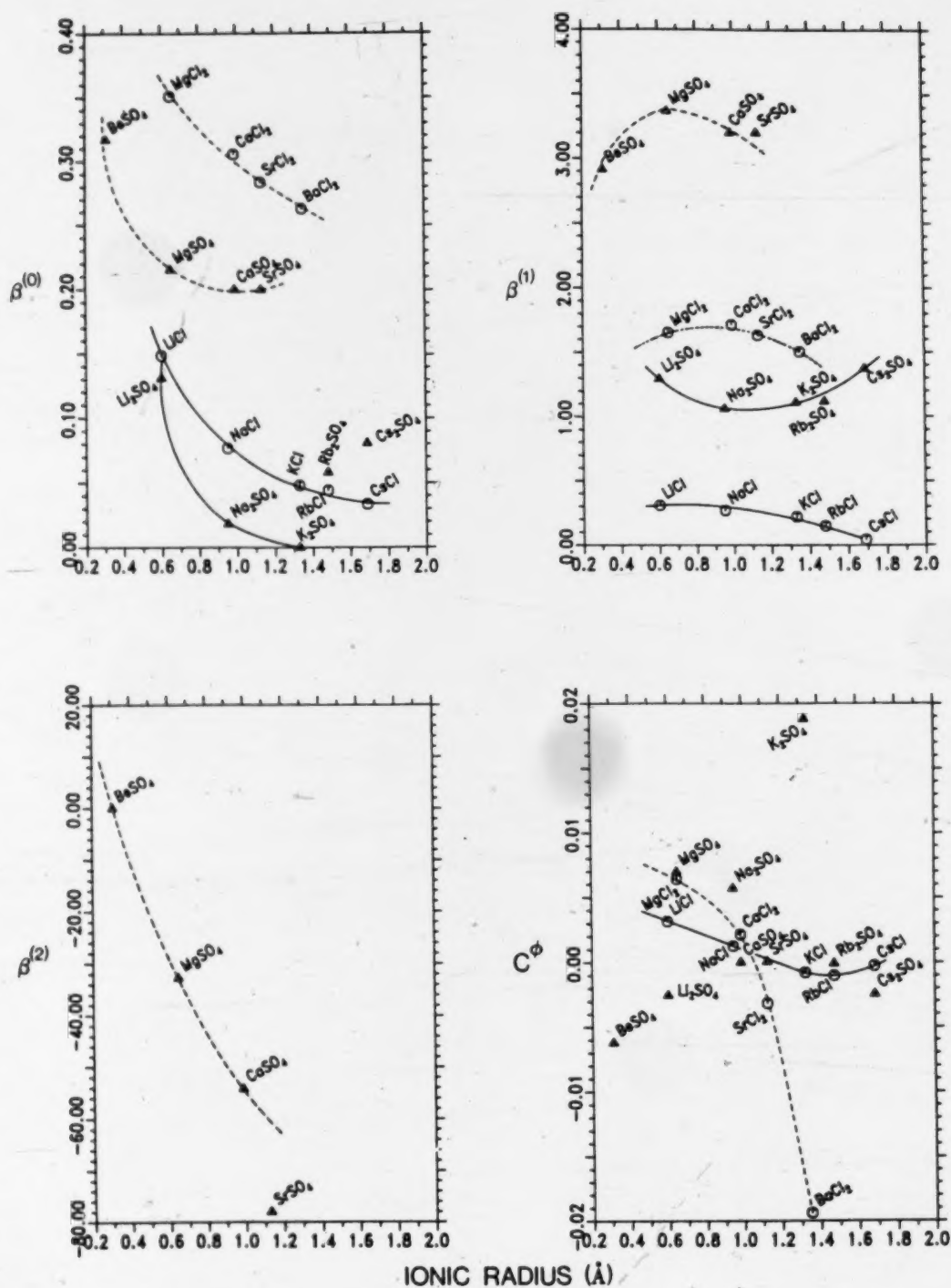


Figure 5. Cation-anion interaction parameters vs. ionic radius of the cation at 25°C, for the chloride and sulphate anionic groups.

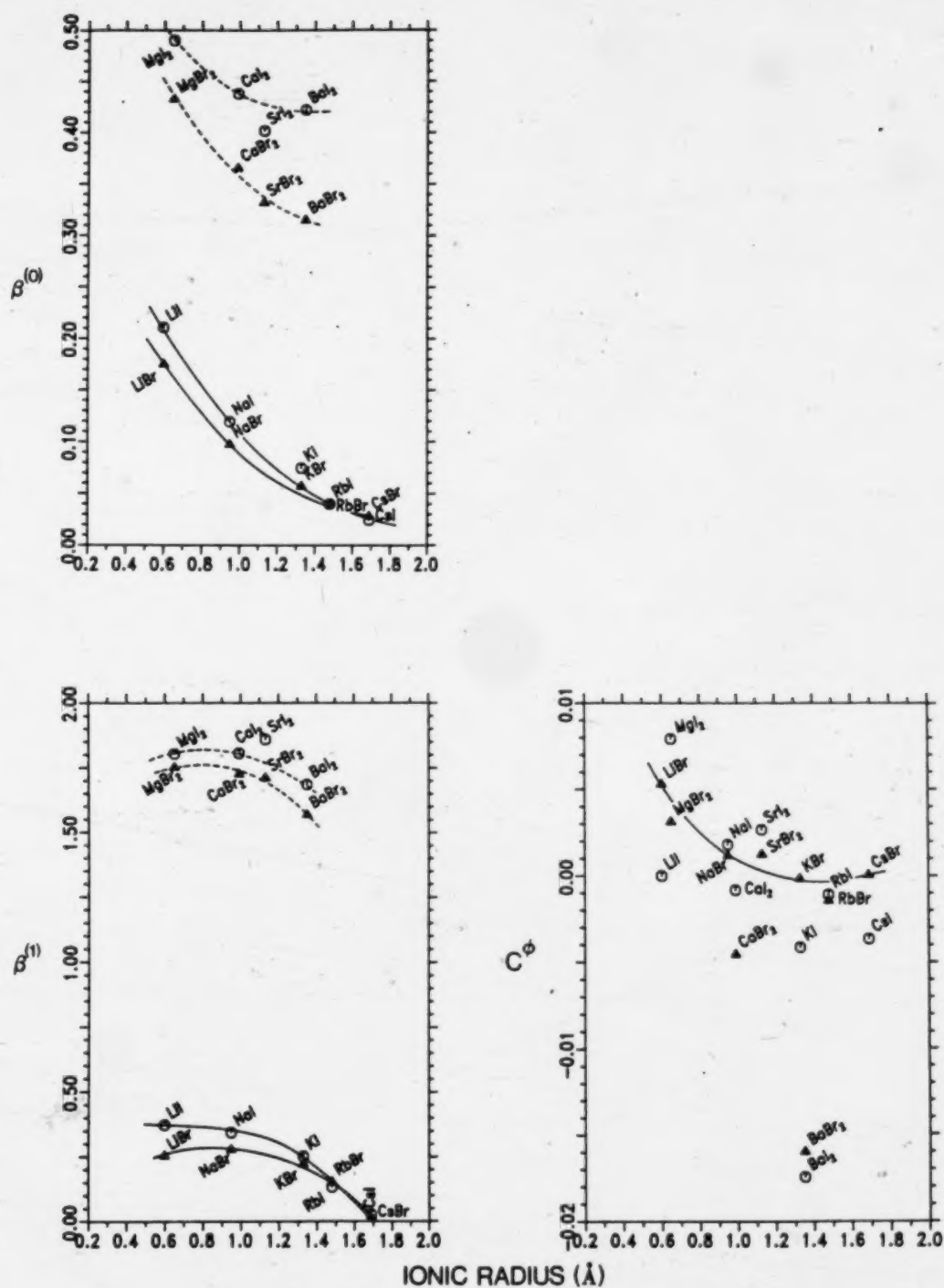


Figure 6. Cation-anion interaction parameters vs. ionic radius of the cation at 25°C, for the fluoride and bromide anionic groups.

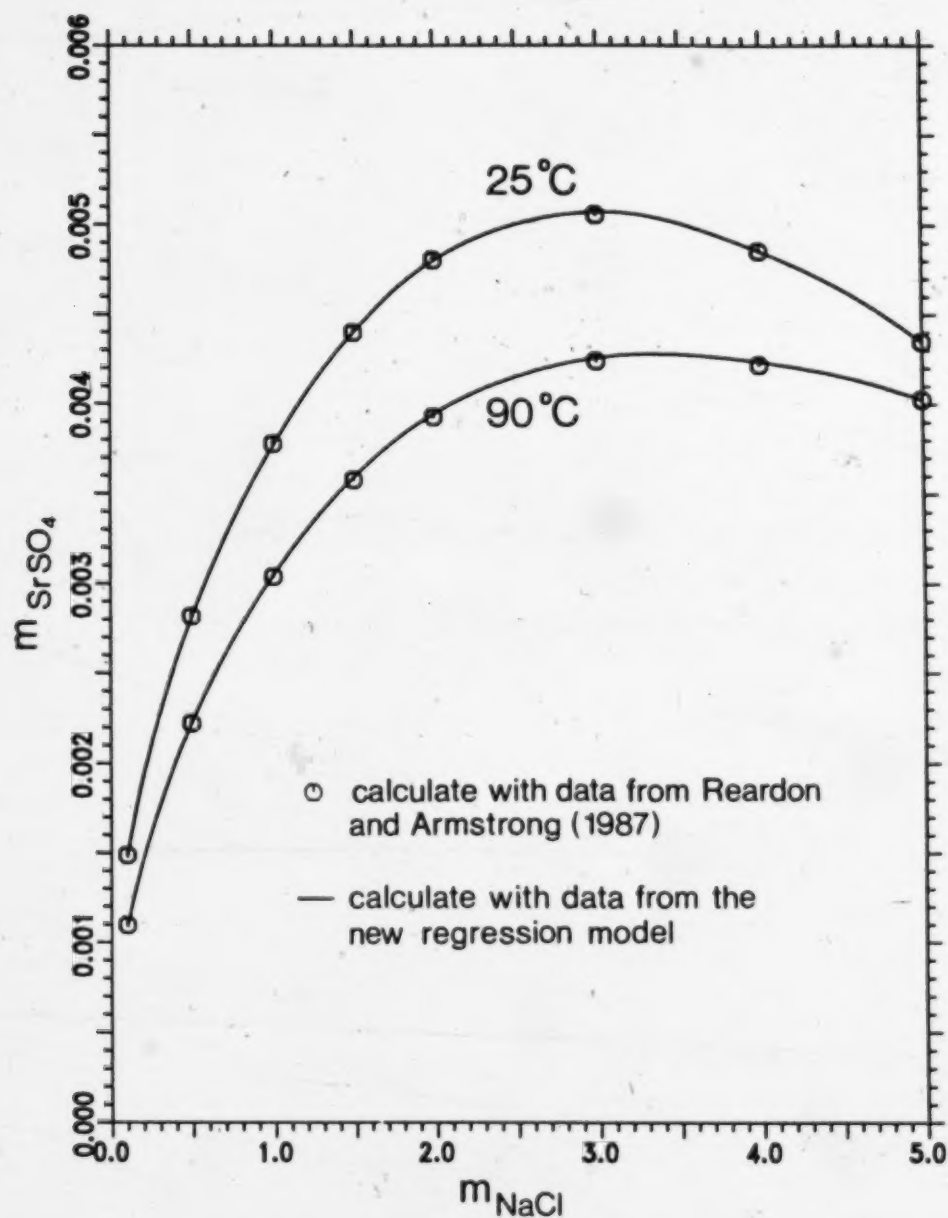


Figure 7. Solubility of celestite as calculated with estimates of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^* from Reardon and Armstrong (1987) and from this study.

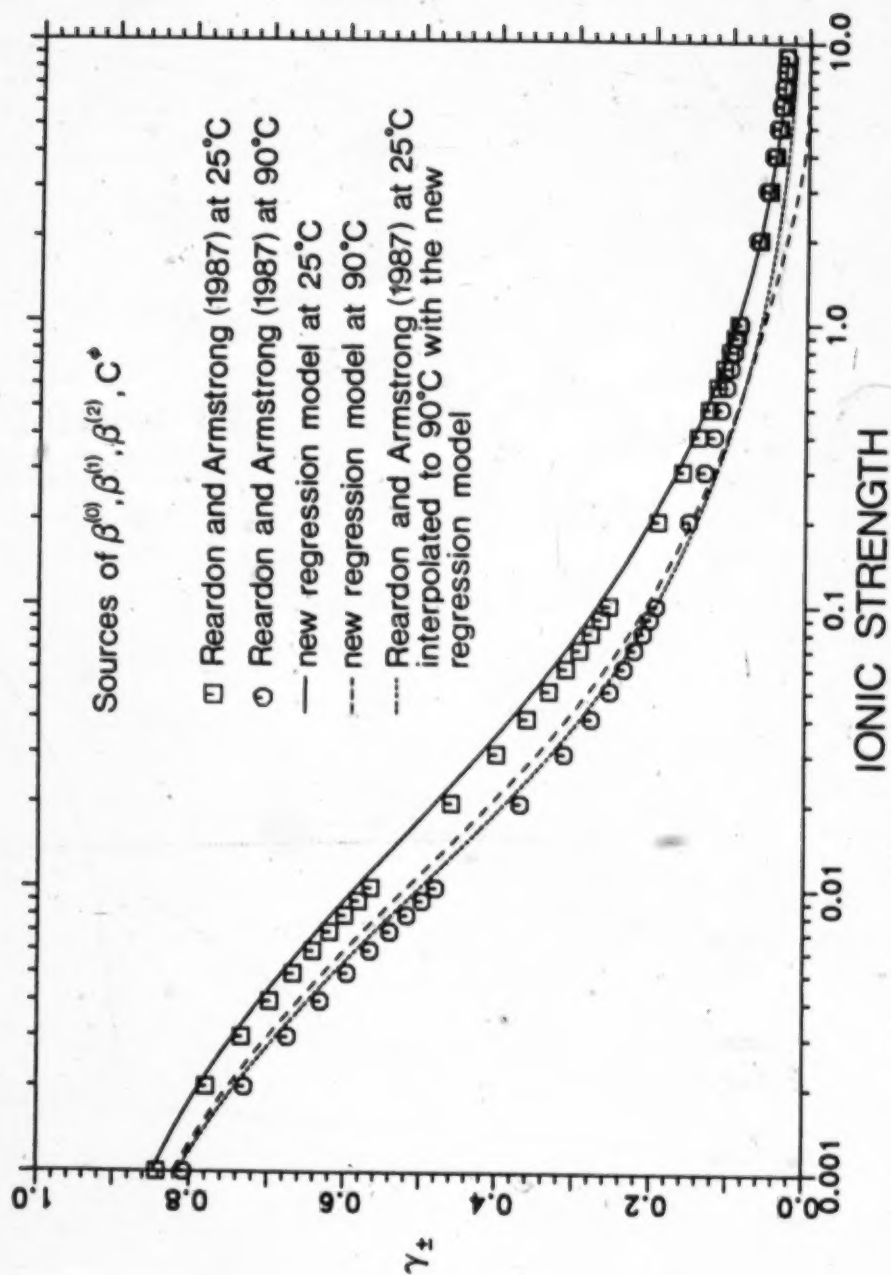


Figure 8. Mean activity coefficients of SrSO_4 in 0.01 to 10.0 m NaCl solutions as calculated with estimates at $\beta^{(0)}, \beta^{(1)}, \beta^{(2)}$ and C^* from Reardon and Armstrong (1987) and from this study.

IV. A MIXING CELL MODEL FOR SIMULATING MASS TRANSPORT AND GEOCHEMICAL REACTIONS IN SEDIMENTARY BASINS

INTRODUCTION

The main focus of this thesis is to develop a model capable of simulating water-rock reactions that occur in clastic sedimentary basins. The previous two chapters described an improved geochemical model suitable for simulations in brines and the data base of thermodynamic parameters required by the geochemical code. The emphasis of this chapter is placed upon the development of first, a hydrogeological model which is designed to transport, disperse and react mass within a two-dimensional groundwater flow regime and secondly, the coupling of this mass transport code with a geochemical reaction model. The applicability of the model to natural systems is demonstrated through a series of sensitivity analyses.

Numerical modelling in contaminant hydrogeology has shifted its focus from the transport of non-reactive contaminants to the transport of reactive components. Mass transport with associated dispersion, diffusion and geochemical reactions is described mathematically by the advection-dispersion equation. This equation, written for a two-dimensional flow system, is (Schwartz and Domenico, 1973):

$$D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} - v_y \frac{\partial C}{\partial y} + \Sigma R_i = \frac{\partial C}{\partial t} \quad (1)$$

where: C = concentration of the solute
D_L = longitudinal dispersion coefficient
D_T = transversal dispersion coefficient
v_x = horizontal component of groundwater velocity
v_y = vertical component of groundwater velocity
R_i = chemical reactions applied to the solute
x = horizontal coordinate direction
y = vertical coordinate direction

t = time

The solution to this equation is typically undertaken using analytical functions or numerical techniques. While analytical solutions are generally easy to use, they are normally limited to very simple systems (e.g. isotropic and homogeneous porous medium, only one solute, one dimensional flow). Numerical methods, such as the finite difference or finite element methods, can account for heterogeneities in natural systems and the complex set of chemical processes within a point to point distribution. However, while numerical codes can simulate much of the complexity inherent in natural systems, hydrogeologists typically can not take full advantage of the model because the considerable field data required to define spatial and temporal variations in the system are typically not available. Solution of the mass transport equation is further complicated by the mathematical framework upon which the separate theories of transport and reactions have evolved. It is difficult to numerically combine the physical processes of advection and dispersion with chemical reactions because transport is described by partial differential equations (and uses units of mass) and reactions are defined by algebraic equations (and uses units of concentration).

The two most common methods for combining the two mathematical methods are the one-step and the two-step procedures (Miller and Benson, 1983). The one-step approach involves incorporating the equations that describe chemical reactions into the partial differential equation which describe transport of mass. The partial differential equation describing mass transport is written as difference equations in space, forming a ordinary differential equation. Because both the ordinary differential equations for transport and the algebraic equations describing reactions have a similar form, they can be grouped into a single set of equations. Concentration is determined by a simultaneous solution of this set of equations to both transport and reaction processes. Examples of models designed to operate with a one-step procedure were developed by Rubin and James (1973), Valocchi et al. (1981) and Jennings et al. (1982).

The two-step approach involves solution of the partial differential equations independently from the algebraic equations during the same time step. Mass is first transported by advection and dispersion, then concentrations are adjusted to account for mass loss or gain through reactions. At the start of a time step, mass is transported along flow lines as defined by the velocity field. The mass is then dispersed by either a random-walk procedure (Ahlstrom et al., 1977, Schwartz and Crowe, 1980) or by a direct solution to the advection-dispersion equation (Grove and Wood, 1979, Schultz and Reardon, 1983, Cederberg et al., 1985). Still within the same time step, the second part of the two-step procedure involves adjusting the mass in solution to account for the geochemical reactions between the species and solid phases. Because the amount of mass reacted depends upon the amount of mass transported, and vice versa, different amounts will be calculated depending upon which process is undertaken first. Thus, to correctly calculate the amount of mass transported and the amount transferred from or to solution, the two-step procedure requires iteration between the two sets of equations. Numerical models employing this approach have been proposed by Schwartz and Domenico (1973), Grove and Wood (1979), Dudley et al. (1981), Schultz and Reardon (1983), Cederberg et al. (1985), Narisimhan et al. (1986) and Schwartz and Milne-Home (1987).

The advantage of the one-step procedure is that it is theoretically more rigorous than the two-step approach. However, due to the computational complexities of coupling the equations, its application is generally limited to one-dimensional flow problems (Miller and Benson, 1983). The one-step model developed by Miller and Benson (1983) can be applied to two- or three-dimensional systems if a two-step procedure is used. Treating the transport and reaction of mass as a two-step procedure is considerably easier to solve by numerical methods, but it is theoretically less rigorous than the one-step approach (Miller and Benson, 1983). The two-step approach is more applicable than the one-step model because it can be extended to two- or three-dimensional flow problems and to systems characterized by very complex hydrogeological conditions. In addition, the two-step procedure is well

defined for coupling existing geochemical reaction codes to existing mass transport models. The major drawback with the two-step model relates to the physical limits of the computer necessary to handle a computer code that simulates the transport and reaction of a multitude of components in a complex multi-dimensional environment. Generally, if the flow system is large and complex, few components can be included. In order to include a wide variety of chemical constituents, the flow system that is considered is generally quite small and simple. In addition, the solution of hydraulic heads, groundwater velocities and hydraulic gradients at each node, and the simulation of chemical reactions within each element, during each iteration and each time step, require enormous computer capabilities.

Mass transport and reaction can also be simulated with mixing-cells. These models are based upon a more simplified version of the advection-dispersion equation. A mixing cell is a geochemical version of a *lumped parameter model*. Lumped parameter models do not consider the spatial variability and heterogeneities which occur within the real world. The numerical methods are generally classified as *distributed parameter models* because they account for heterogeneities and spatial variations on a point to point distribution. Hence, the lumped parameter models are not as theoretically rigorous the distributed parameter models. A lumped parameter model incorporates simplifications that allow approximations of certain aspects of a physical system to permit realistic interpretations within a spatially and temporally averaged context. In addition, because they are (1) conceptually simple, (2) require fewer characterizing parameters and (3) use considerably less computer time, lumped parameter models present an attractive alternative to the distributed parameter methods for mass transport modelling.

The model developed in this chapter is based upon the lumped parameter theory. The model is designed to transport, disperse and react mass within a two-dimensional groundwater flow system. The advection, reaction, dispersion and diffusion of mass is performed with mixing cells.

MIXING CELL THEORY

Lumped parameter models are basically "black-box" models. These models reproduce certain observed behaviours of a system without providing details of the physical framework and processes occurring within the physical system. Lumped parameter models are used primarily where the variations within a system (both spatially and temporally) are so small that they can be averaged into a single representative homogeneous parameter, and where the responses of the natural system are assumed to occur instantaneously. Physical and chemical parameters that are lumped into hydrogeological mixing cells include aquifer geometry, aquifer structure, anisotropism, heterogeneities of permeability and storativity, mixing processes, geochemical reactions and the distribution of recharge. Within each cell the concentration of the solute is assumed to be uniform (no concentration gradients) and the volume occupied by the solute is assumed negligible. Therefore, if these conditions apply to a particular setting, and if the purpose of the modelling exercise is to obtain a set of responses, then the lumped parameter approach is acceptable. However, if the complexities of the physical and chemical framework of the system are large, or if information concerning both the processes involved during the transport and the final responses are required, then a distributed parameter model should be used. When considering the applicability of a lumped parameter model, it is necessary to assess first, the degree to which spatial heterogeneities can be neglected, and second, the degree to which the physical and chemical processes which act on the solute can be represented by a single lumped process.

Lumped parameter models are often applied to natural systems because the processes are too complex and the reliability of data too uncertain for a complete mathematical formulation. In chemical process engineering, lumped parameter models (known as reactor vessel or stir tanks) are used to simulate the mixing of chemicals in large mixing tanks (Himmelblau and Bischoff, 1968). Lumped parameter models are also widely used in hydrology where these models (known as routing models) are basically an

extension of the water balance and used to consider possible paths taken by water as it moves through the hydrological cycle. Models of this type that are specifically designed to address the groundwater component of the water balance were developed by Crowe and Schwartz (1981a, 1981b, 1985), Senarath and Rushton (1984) and Crosby et al. (1985). Lumped parameter models have also seen limited application in hydrogeology, with most studies focusing upon the transport and decay of isotopes as a means of age-dating the groundwater flow system (Przewlocki and Yurtsever, 1975; Simpson and Duckstien, 1975; Małoszewski and Zuber, 1982; Llamas et al., 1982; Małoszewski et al., 1983; Campana and Simpson, 1984; Campana and Mahin, 1985).

Because mixing cell models use a "black box" approach and do not explicitly handle dispersion, these models have been classified into several groups on the basis of how they represent the routing, dispersing and mixing of mass within a cell. The most commonly used models include:

1. *Piston Flow Model*: which represents no mixing between fluid entering the cell and that currently occupying the cell;
2. *Well-mixed Model*: which assumes complete mixing between the fluid entering the cell and that presently occupying the cell;
3. *Modified Mixing Cell Model*: which accounts for a mixing process between that of the Piston Flow Model and the Well-mixed Model;
4. *Dispersive Model*: which simulate fluid mixing with an analytical solution to the dispersion equation.

The basic equation upon which the theory of lumped parameter models, including the mixing cell, is based is the mass balance equation:

$$\zeta_t = \zeta_{t-1} + \zeta_{IN} - \zeta_{OUT} + \sum R_i \quad (2)$$

where: ζ_t = mass within a cell during the present time step
 ζ_{t-1} = mass within a cell during the previous time step

- ζ_{IN} = amount of mass entering a cell
 ζ_{OUT} = amount of mass leaving a cell
 R_i = chemical reactions applied to the mass

The piston flow model simulates the movement of mass by the concurrent displacement of the fluid presently occupying a cell by an incoming fluid. This displacing process implies that the model does not account for mixing (hence, the only change in the concentration of a solute occurs due to reactions). Thus, it is not generally applicable to groundwater studies. However, it does provide the basis from which more complex mixing cell models are developed. Figure 1a illustrates the operation of the piston flow model. The piston flow model simulates the amount of water that is displaced from a cell to be equal in volume to that entering the cell, and both are equal to the volume of water within a cell. The concentration of the fluid that is displaced from the cell is the same as that currently occupying the cell. Mathematically, this is expressed as:

$$C_i = C_{IN} \quad (3)$$

$$C_{OUT} = C_{i-1} \quad (4)$$

$$V_{OUT} = V_{IN} = V \quad (5)$$

- where:
- C_i = concentration of the solute in a cell during the present time step
 - C_{IN} = concentration of the solute entering the cell
 - C_{OUT} = concentration of the solute leaving the cell
 - C_{i-1} = concentration in a cell during the previous time step
 - V_{OUT} = volume of groundwater flow out of a cell
 - V_{IN} = volume of groundwater flow into a cell
 - V = volume of the cell

The well-mixed model accounts for complete mixing between the fluid currently occupying a cell and that flowing into the cell. However, this model also is not generally applicable to groundwater studies unless the cells are relatively small or the inputs and

outputs are distributed over a large area. The well-mixed model assumes instantaneous volumetric expansion of the cell to accommodate the additional input of fluid, instantaneous complete mixing and instantaneous discharge of fluid with a volume equal to the volume of inflow. The concentration of the fluid which is discharged is equal to the new concentration of the fluid in the cell (Figure 1b). These processes are expressed as:

$$C_1 = \frac{VC_{t-1} + V_{IN}C_{IN}}{V + V_{IN}} \quad (6)$$

$$C_{OUT} = C_1 \quad (7)$$

$$V_{OUT} = V_{IN} \quad (8)$$

Because natural systems lie in between these two models, the modified mixing cell was developed by incorporating properties of both. Based on the piston flow model theory, incoming fluid displaces fluid presently occupying the cell and again the volume of the cell remains constant (Figure 1c). However, the volume of water entering a cell is less than the volume of the cell. The concentration of water that is displaced from the cell is the same as that occupying the cell. Once a new fluid has been added to the cell and some of the existing fluid is displaced, complete mixing between the two fluids in the cell occurs. Because some of the original fluid has been displaced from the cell, mixing will not be as complete as in the well-mixed model. The new concentration within the cell is calculated by:

$$C_1 = \frac{V_{IN}C_{IN} + (V - V_{OUT})C_{t-1}}{V + V_{IN} - V_{OUT}} \quad (9)$$

Because the volume of water that is displaced from a cell is equal to that entering the cell, equation (9) becomes:

$$C_1 = \frac{V_{IN}C_{IN} + (V - V_{IN})C_{t-1}}{V} \quad (10)$$

The volume of discharge from the cell and its concentration is:

$$V_{OUT} = V_{IN} \quad (11)$$

$$C_{OUT} = C_{t-1} \quad (12)$$

The degree of mixing within each cell is defined by a mixing factor. A value of 0 indicates no mixing, and values approach 1 as the mixing process becomes increasingly complete. The mixing factor is calculated by :

$$\Gamma = \frac{V - V'_{OUT}}{V} \quad (13)$$

where: Γ = degree of mixing parameter
 V'_{OUT} = volume of discharge from a cell before mixing

In this formula, a well mixed model will have V'_{OUT} equal to 0, a piston flow model will have V'_{OUT} equal to V_{OUT} , and a modified mixing cell model will have a value between 0 and V_{OUT} .

Real systems have been represented by either a single mixing cell or as a series of discrete but interconnected mixing cells. The single mixing cell model is the more traditional approach and generally involves representing an entire aquifer or flow system by a single mixing cell. For example, Gelhar and Wilson (1974) and Mercado (1976) have used a single mixing cell model to represent an entire aquifer for studies of impact of de-icing salt on groundwater quality, and nitrate and chloride contamination of a coastal aquifer, respectively.

Models comprised of several connected cells are known as *discrete compartment models* (Simpson and Duckstein, 1975) or *finite state mixing cell models* (Maloszewski and Zuber, 1982). These models, illustrated by Figure 2, are basically just an extension of

the single mixing cell model formed by coupling single cells in a series along the proposed flow path. This allows mass to be transported from one cell to the next, or from one part of the flow regime to an adjacent area. The major drawback of this model is a knowledge of the groundwater flow regime in order to align the cells in the direction of groundwater flow. A set of recursive equations are defined to describe the transport and mixing and are solved at each iteration in time as the solute moves through the mixing cells. Discharge from an upstream cell will provide the input for the next downstream cell. Thus:

$$V_{i,OUT} = V_{i+1,IN} \quad (14)$$

$$C_{i,OUT} = C_{i+1,IN} \quad (15)$$

where: $V_{i,OUT}$ = volume of groundwater flow out of the upstream cell
 $V_{i+1,IN}$ = volume of groundwater flow into the downstream cell
 $C_{i,OUT}$ = concentration of the solute discharge from the upstream cell
 $C_{i+1,IN}$ = concentration of the solute entering the downstream cell

Discrete-state compartment models represent a significant advancement from the single cell mixing cell models. By representing the groundwater flow system as a series of cells, and by incorporating simple routing and mixing equations, the discrete-state compartment model eliminates the need for a complex solution to the set of differential equations defining the advection-dispersion equation. Because each cell represent a specific section of the flow regime, different hydrogeological and hydrochemical parameters may be assigned to each cell. As the number of cells increases, the representative volume of a cell decreases, and the number of parameters used to characterize each cell increases, these lumped models essentially become distributed parameter model with some parameters lumped.

Mixing cells are designed to represent the physical transport of mass through a natural system. But because they are lumped representations of chemical processes, they do

not consider actual time for the transport of fluids or dissolved mass in units such as days or years. Rather lumped parameter models mimic time by utilizing a parameter to control or route mass among the cells. These parameters are known by several names such as the *delay parameter* (Senarath and Rushton, 1984), the *boundary recharge fraction* (Przewlocki and Yurtsever, 1974; Simpson and Rushton, 1984) and the *boundary recharge volume* (Campana and Simpson, 1984). In all cases these parameters are the lumped analogies to the physical quantities of permeability, groundwater velocities and spatial dimensions of an aquifer that are associated with distributed parameter models. It is an integral part of the discrete-state compartmental models because it controls not only the routing of mass between cells from one time step to the next, but also during a time step.

The delay parameters are obtained by making an initial estimate based on a knowledge of the actual flow direction, the travel time, groundwater velocities, etc., and calibrated through a trial and error technique of matching the simulated responses to field observations. Increasing the number of cells allows for representation of a more complex system. However, this also increases the number of delay parameter that must be fit. As is the case with any regression problem, given enough fitting parameters, any data can be made to fit the observations and the standard error of fit generally decreases. However, as noted by Małozzewski and Zuber (1982), the physical significance of addition delay parameters is in doubt and a model comprised of more parameters is less reliable than one with fewer parameters.

The two main problems associated with applying lumped parameter models and mixing cells to simulations of mass transport in groundwater flow regimes are (1) inferring the flow path and (2) approximating transit times through the cells by a delay parameter. Typically these problems are overcome by guessing at an initial flow direction and values of the delay parameters and then modifying the initial estimates through an initial trial and error calibration process. However, because of the number of parameters involved in the

simulation, the solution may not be unique. The lumped parameter models would be accurate if the flow direction and transport times were known.

One method that has proven useful in resolving this dilemma is to determine the position of flow lines with a distributed parameter model (e.g. either a finite element or finite difference technique) and then align the mixing cells along these flow lines. Initial attempts to do this in one dimension by Dance and Reardon (1983) and in a two-dimensional cross section by Llamas et al. (1982) have been successful. Also, because the position of the cells are defined by the flow lines, the groundwater velocity, and hence transit times, across each cell can be accurately determined. Two advantages of this technique are (1) there is no groundwater flow or advective mass transport across the flow lines boundaries of the mixing cells, thus reducing the number of transport delay parameters which must be defined, and (2) the model presents the groundwater regime in a more physically realistic framework.

This technique still does not eliminate the problem of mass transport across the stream line boundaries (due to transversal dispersion and diffusion). The concept of a *dead space* or *dead cells*, which was introduced by Simpson and Duckstein (1975), consists of incorporating special cells into the discrete-state compartment models to allow the simulation of the lateral transfer of mass out of a flow system or across flow lines (Figure 3). These dead cells, which represent a stagnant part of the groundwater regime, will accept the transfer of mass between them and the active cells without a net exchange of water. A fraction of water and associated mass from an active cell enters a dead cell where it mixes with the fluid currently in the dead cell. Then an equal volume of water, accompanied by mass, from the dead cell flows back into the active cell. Because the volume of water exchanged between an active cell and a dead cell is equal, there is no net change in the volume of water in the active cell. But because the concentration of these two cells are different, there is a net change in the mass transferred and hence, a change in the the concentration of the active cell. This technique has been applied to discrete-state

compartment models by Simpson and Duckstein (1975), Llamas et al. (1982), Campana and Simpson (1984) and Campana and Mahin (1985). Llamas et al. (1982) represented the mass transport across flow line boundaries by exchanging 0.1% (determined through sensitivity analyses) of the smaller of the two volumes in adjacent cells. In all models, the parameters controlling mass transfer from active cells during each time step was determined by a trial and error procedure.

DESCRIPTION OF THE MODEL

The model described in this section is based on a multi-cell approach, similar in concept to the discrete-state compartment model. Series of interconnected cells are formed to enable the simulation of mass transport and reaction in a two-dimensional groundwater flow regime. The steps undertaken to form the mixing cell model are:

1. use a groundwater flow model to determine the position of stream lines and stream tubes in a two-dimensional cross section;
2. determine the x- and y-coordinates of all points along the stream lines and calculate the groundwater velocity at each of these points;
3. use these velocities to calculate the distance that advective transport will move mass along a stream line during a predefined interval of time;
4. divide the stream tube into a series of mixing cells, with each cell having an upper and lower boundary located along the stream lines and lateral boundaries located at the distance previously determined by the transport during the predefined time intervals;
5. define initial geochemical conditions within each cell and introduce mass into the first cell;
6. move mass through the cells by advection and dispersion, and redistribution mass between the minerals and dissolved components through reaction.

Formulation of the Advection-Dispersion Mass Transport Model

The first step of the modelling procedure is to construct a groundwater flow model capable of transporting mass by advection and distributing it among the cells by dispersion, within a two-dimensional groundwater flow system. Because the primary interest of this study focuses upon the transport of mass rather than patterns of groundwater flow, the model developed here calculates stream function values rather than hydraulic heads. Groundwater velocities can be directly calculated from stream function values and it is the velocity terms (equation (1)) which control the transport of mass. Further numerical advantages of a groundwater flow code that calculates stream function values rather than one that calculates hydraulic potentials are, as discussed by Frind and Matanga (1985):

1. the flow paths, and hence the direction of mass transport, is shown directly by contouring the calculated stream function values;
2. the calculated velocities in systems characterized by a very small hydraulic gradient are more accurate when calculated with the stream function model because of less roundoff error during the computer calculations;
3. the boundary fluxes are calculated directly and hence, are more accurate than those calculated with a model which calculates hydraulic potential.

The main limitation of the stream function model is that it is typically limited to steady state groundwater flow. Because groundwater flow systems in large sedimentary basins are typically assumed to be at steady state (Toth, 1963, Freeze and Witherspoon, 1966, Hitchon, 1969, 1984), have a small gradient along the water table in relation to the size of the flow regime (Toth, 1963, Freeze and Witherspoon, 1966, Hitchon, 1969) and the fluxes along the water table control the flow system (Toth, 1963, Freeze and Witherspoon, 1966, 1967, Hitchon, 1969, 1984), the stream function model is applicable for this studies.

The basis for the theory of the stream function model is described by Frind and Matanga (1985) and only a brief discussion is presented here. The reader is referred to

Figure 4 for an illustration of the terminology and concepts presented during the following derivation of the stream function equations. Typically, a groundwater flow model will calculate values of hydraulic potential. The equation of flow used to calculate hydraulic potential for flow under steady state conditions and through a two-dimensional anisotropic porous media is:

$$\frac{\partial}{\partial x} \left(K_{xx} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial \phi}{\partial y} \right) = 0 \quad (16)$$

where: K_{xx} = horizontal hydraulic conductivity
 K_{yy} = vertical hydraulic conductivity
 ϕ = hydraulic potential
 x, y = coordinate directions

This equation assumes that the principal directions of permeability are parallel to the two coordinate axes.

The stream function equations are derived by Frind and Matanga (1985) on the basis of the flux along the stream lines. The governing equation for stream functions, analogous to equation (16) is:

$$\frac{\partial}{\partial x} \left(\frac{1}{K_{yy}} \frac{\partial \Psi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{1}{K_{xx}} \frac{\partial \Psi}{\partial y} \right) = 0 \quad (17)$$

where: Ψ = stream function value

By definition, the stream function value (Ψ) is constant along a stream line. Specific discharge through a section of a stream tube, which is defined as the bounded by two adjacent flow lines, is calculated by:

$$q = \frac{\Delta \Psi}{\Delta p} \quad (18)$$

where: q = specific discharge
 $\Delta\Psi$ = change in the stream function value between adjacent flow lines
 Δp = perpendicular distance across the stream tube

In an x - and y -coordinate system the perpendicular distance across the stream tube (Δp) is calculated as the difference between the x - and y -coordinates along the two bounding stream lines. Mathematically, this can be expressed as:

$$\Delta p = \sqrt{\Delta x^2 + \Delta y^2} \quad (19)$$

where: Δx = horizontal distance between points each on a bounding stream lines
 Δy = vertical distance between points each on a bounding stream lines

The fluid velocity through the cross section is therefore:

$$v = \frac{\Delta\Psi}{\theta\Delta p} \quad (20)$$

where: v = average linear groundwater velocity
 θ = porosity

The distance traveled along a stream line during a specific interval of time is:

$$\Delta s = v\Delta t \quad (21)$$

where: Δs = distance traveled during a time interval
 Δt = specific time interval

Substituting equation (20) into equation (21) produces an expression for the distance traveled as a function of the change in the stream function value and the cross-sectional area of the stream tube (Frind and Matanga, 1985):

$$\Delta s = \frac{\Delta \Psi}{\theta \Delta p} \Delta t \quad (22)$$

The quantity of water passing through any cross-sectional segment of the stream tube is constant. However, the fluid velocity changes because the distance between bounding streamlines change along the length the stream tube. Therefore, the width of the stream tube (Δp) is a function of the position (s) along the stream tube, and thus, the fluid velocity (v) is a function of the width of the stream tube. The total distance traveled along a stream tube during a specific interval of time (Δt) is calculated by:

$$\Delta s = \frac{\Delta t \Delta \Psi}{\theta} \int \frac{1}{\Delta p(s)} ds \quad (23)$$

Examples of stream lines calculated and plotted with the programs for a homogeneous and in a layered system are illustrated by Figure 5. Because a stream tube confines flow to the longitudinal direction, advective transport of mass (i.e. no dispersion) is also restricted to the stream tube. The distance that mass will travel by advective transport alone is determined by integrating over the groundwater velocities along the stream line during a specific time interval (equation (23)). Given a specific interval of time (Δt), the flow lines are divided into a series of segments of different lengths but all having equal advective transport times. Taking this procedure one step further, a series of cells are constructed by dividing the stream tube into a number of segments all having equal transit times. Because the cells are formed within a stream tube, which confines the advective transport of mass, all mass will move from an upstream cell to a downstream cell during a time step. Also, because the adjoining boundaries of the cells are located at intervals of Δt , advective transport will transfer all the mass within each cell successively downstream to the next cell at the start of each time step.

The total transit time along each flow line increases as the stream lines move deeper into the flow regime because the length of the flow line increases. Therefore, there will be more intervals of equal Δt along the lower boundary of the stream tube than along the upper boundary. Hence, the series of cells bounded by Δt and the two stream lines will be increasingly distorted along the stream tube. This problem has been eliminated by assuming the existence of a hypothetical stream line which is centrally located within the stream tube. Rather than divide the bounding stream lines into intervals of Δt , the central stream line is divided into segments at intervals of Δt (Figure 4). The upper and lower flow lines are then divided into the same number of segments. However, to have the same number of segments along both the upper, lower and central stream lines, the transit time for an upper and a lower segment can no longer be equal to Δt . The number of intervals of Δt along the hypothetical stream line is determined as an average of the total transit times along the upper and lower stream lines:

$$n_c = \frac{t_u + t_l}{2 \cdot \Delta t} \quad (24)$$

where: n_c = number of cells within the stream tube
 t_l = total transit time along the upper stream line
 t_u = total transit time along the lower stream line

The size of the actual time intervals along the upper and lower stream lines are calculated by:

$$\Delta t_u = \frac{t_u}{n_c} \quad (25)$$

$$\Delta t_l = \frac{t_l}{n_c} \quad (26)$$

where: Δt_u = time interval along the upper stream line
 Δt_l = time interval along the lower stream line

The size of the time intervals along the lower and upper flow tube boundaries are slightly greater than and slightly less than Δt , respectively. However, the actual transit time for mass transport through a cell is actually an average of the transit times along the upper and lower stream lines (equation (24)), and this average equals Δt . The resulting series of cells is illustrated by Figure 6.

Because the mixing cells are arranged parallel to the direction of groundwater flow, a mathematical derivation of the delay parameters can be obtained from the advection-dispersion equation as follows. Equation (1), (without reactions) written in standard finite difference notation is:

$$\begin{aligned} \frac{C_{t,i,j} - C_{t-1,i,j}}{\Delta t} = & -v_x \left(\frac{C_{t-1,i,j+1} - C_{t-1,i,j-1}}{\Delta x} \right) - v_y \left(\frac{C_{t-1,i,j+1} - C_{t-1,i,j-1}}{\Delta y} \right) + \\ & D_L \left(\frac{C_{t-1,i,j+1} - 2C_{t-1,i,j} + C_{t-1,i,j-1}}{\Delta x^2} \right) + \\ & D_T \left(\frac{C_{t-1,i,j+1} - 2C_{t-1,i,j} + C_{t-1,i,j-1}}{\Delta y^2} \right) \end{aligned} \quad (27)$$

- where:
- $C_{t-1,i,j}$ = concentration at a downstream point during previous time step
 - $C_{t-1,i,j}$ = concentration at a central point during the previous time step
 - $C_{t-1,i+1,j}$ = concentration at an upstream point during previous time step
 - $C_{t-1,i,j-1}$ = concentration at a downstream lateral point during the previous time step
 - $C_{t-1,i,j+1}$ = concentration at an upstream lateral point during the previous time step
 - $C_{t,i,j}$ = concentration at a central point during the present time step
 - Δt = size of the time step
 - Δx = horizontal distance between points
 - Δy = vertical distance between points

The terms of equation (27) are rearranged as:

$$\begin{aligned}
C_{i,j} - C_{t-1,i,j} = & -\frac{v_L \Delta t}{\Delta x} (C_{t-1,i,j} - C_{t-1,i-1,j}) - \frac{v_T \Delta t}{\Delta y} (C_{t-1,i,j} - C_{t-1,i,j-1}) + \\
& \frac{2D_L \Delta t}{\Delta x^2} \left(\frac{C_{t-1,i-1,j}}{2} - C_{t-1,i,j} + \frac{C_{t-1,i+1,j}}{2} \right) + \\
& \frac{2D_T \Delta t}{\Delta y^2} \left(\frac{C_{t-1,i,j-1}}{2} - C_{t-1,i,j} + \frac{C_{t-1,i,j+1}}{2} \right)
\end{aligned} \quad (28)$$

Equation (28) can be written in terms of the mixing cell model. The horizontal and vertical distance between points is replaced by the distance across the cell in the direction parallel and perpendicular to the direction of flow, respectively (Figure 4). Because the cells are parallel to the direction of flow, and stream lines form the upper and lower boundaries of the cells, there will not be advective transport across these stream line boundaries (i.e. $v_T = 0$). Thus, equation (14) written in terms of the mixing cell model becomes:

$$\begin{aligned}
C_{i,j} - C_{t-1,i,j} = & -\frac{v_L \Delta t}{\Delta l} (C_{t-1,i} - C_{t-1,i-1}) + \frac{2D_L \Delta t}{\Delta l^2} \left(\frac{C_{t-1,i-1}}{2} - C_{t-1,i} + \frac{C_{t-1,i+1}}{2} \right) + \\
& \frac{2D_T \Delta t}{\Delta p^2} \left(\frac{C_{t-1,i,j-1}}{2} - C_{t-1,i,j} + \frac{C_{t-1,i,j+1}}{2} \right)
\end{aligned} \quad (29)$$

where: Δl = width of a mixing cell, parallel to the direction of flow
 Δp = width of the mixing cell, perpendicular to the stream lines
 v_L = groundwater velocity parallel to the direction of flow

A lumped parameter advection term (or delay parameter) is obtained from equation (29) as:

$$\xi_L = -\frac{v_L \Delta t}{\Delta l} \quad (30)$$

where: ξ_L = longitudinal advective delay parameter

Lumped parameter dispersion terms also can be obtained from equation (29):

$$\chi_L = \frac{2D_L \Delta t}{\Delta l^2} \quad (31)$$

$$\chi_T = \frac{2D_T \Delta t}{\Delta p^2} \quad (32)$$

where: χ_L = longitudinal dispersive delay parameter
 χ_T = transversal dispersive delay parameter

The lumped parameter advection term and the lumped parameter dispersion terms are essentially Courant and Peclet numbers, respectively and, as will be discussed later will discussed later, these numbers determine the criteria for stability of the solution.

Substituting equations (30) to (32) into equation (29) yields:

$$C_{i,j} = C_{i-1,j} + \xi_L (C_{i-1,i} - C_{i-1,i-1}) + \chi_L \left(\frac{C_{i-1,i-1,i} - C_{i-1,i,j}}{2} + \frac{C_{i-1,i+1,i}}{2} \right) + \chi_T \left(\frac{C_{i-1,i,i-1} - C_{i-1,i,j}}{2} + \frac{C_{i-1,i,i+1}}{2} \right) \quad (33)$$

The advective transport term of equation (33) can be decoupled from the dispersive transport terms of equation (33) to form two equations representing the transport processes. The decoupling procedure basically involves, first, using the advection transport equation to move all the mass from one cell to the next downstream cell at the beginning of a time step, and secondly, the dispersing of mass among the cells is undertaken with the dispersive equation. The transport processes can be decoupled because of the manner in which the common boundaries of the mixing cells within a stream tube are derived. These boundaries are located at a distance that mass will travel, by advection only, during a time step. Hence, all mass, regardless of where it is within a mixing cell, will be moved to the next downstream cell at the beginning of each time step. Because this procedure is handled internally by the code, only the dispersive portion of the mass transport equation is solved during each time step. By decoupling the advective transport of mass from the dispersion

processes, a procedure is developed which is not only simpler computationally, but is also numerically more accurate than many existing codes (Schwartz and Milne-Home, 1987) because of a dramatic reduction in the number of numerical calculations.

The two decoupled equations are written as follows. Considering just advective transport, equation (33) simplifies to:

$$C_{t,i} = (1 - \xi_L)C_{t-1,i} + \xi_L C_{t-1,i-1} \quad (34)$$

Equation (34) is analogous to equation (10) when the following variables are equated:

$$C_{t-1,i-1} = C_{IN}$$

$$\xi_L = \frac{V_{IN}}{V}$$

In the same manner in which the advective delay parameters for routing mass among cells were derived from the advection-dispersion equation, lumped parameter dispersion terms can also be obtained. Considering just the dispersive terms of equations (33) yields:

$$C_{t,i,j} = (1 - \chi_L - \chi_T)C_{t-1,i,j} + \frac{1}{2}\chi_L(C_{t-1,i-1,j} + C_{t-1,i+1,j}) + \frac{1}{2}\chi_T(C_{t-1,i,j-1} + C_{t-1,i,j+1}) \quad (35)$$

In a one-dimensional groundwater flow regime, equation (35) is simplified to:

$$C_{t,i} = (1 - \chi_L)C_{t-1,i} + \frac{1}{2}\chi_L(C_{t-1,i-1} + C_{t-1,i+1}) \quad (36)$$

Equation (36) is very similar to the dispersive transport model proposed by Dance and Reardon (1983):

$$C_{t,i} = \lambda C_{t-1,i} + \frac{1 - \lambda}{2}(C_{t-1,i-1} + C_{t-1,i+1}) \quad (37)$$

where: $\hat{\lambda}$ = dispersive factor (Dance and Reardon (1983)) or
lumped parameter dispersive factor

Their model (equation (37)) is the same as equation (36) when the dispersive delay parameter is replaced by the lumped parameter dispersion factor through the following change of variables:

$$\hat{\lambda} = 1 - \chi_L \quad (38)$$

Because the lumped parameter dispersive factor ($\hat{\lambda}$) is restricted to values between 0 and 1, it represents in effect, a percentage of mass remaining in a cell following dispersion. A value of 0 indicates that all mass is dispersed from the cell and a value of 1 indicates that no dispersion will occur. Due to the success obtained by Dance and Reardon (1983) with their model, equation (37) has been adopted as the form of our dispersive model.

The preceding discussion illustrates how the delay parameters used by lumped parameter models relate to the hydrogeological variables used by distributed parameter models. Thus, while lumped parameter and mixing cell models are conceptually and mathematically simple, they are based on the advection-dispersion equation. The model, in effect, determines the value of the lumped parameter advection term by choosing a cell size, when the size of the time step and a calculated velocity field are provided by the model user. The delay parameter for advective transport is a function of the groundwater velocity, size of the time step and size of the mixing cell. Because these three variables are lumped and act as a single term within a lumped parameter model, the stability of the solution with respect to mass transport is a function of the relationship among these three variables. Current lumped parameter models require that the user arbitrarily choose values of (1) the delay parameter, (2) the size of the mixing cells, (3) the size of the time step, and (4) the direction of groundwater flow. Hence, a typical choice of the delay parameter may not be either physically or numerically accurate. The same relationship holds true for the

dispersive lumped parameter, which is a function of the dispersion coefficient, size of the time step and size of the mixing cells.

✓ Formulation of the Coupled Transport and Reaction Model

The most critical stage of the development of the transport and reaction model is to couple the geochemical code with the transport model. A coupled model represents a significant improvement over current quantitative techniques which use only a geochemical code, such as *EQ3/6* (Wolery, 1979), *SOLMNEQ* (Kharaka and Barnes, 1973) or *PHREEQE* (Parkhurst et al., 1980), for simulating mineral reactions in groundwater flow systems. This improvement is due to the ability of our model to simulate not only mass transfer between mineral phases and aqueous components, but also to simulate the important physical transport processes that strongly affects these reactions. The geochemical model, its accompanying data base of thermodynamic parameters and the verification of the model have been discussed in previous chapters. The mathematical methods for coupling the geochemical reaction code to the mass transport code are discussed in this section.

The approach taken here is to use the two-step procedure previous discussed at the beginning of this chapter. The first step involves the advective transport of mass from one cell to another at the beginning of each time step, followed by the dispersal of mass among the cells. The second step, undertaken independently of the first, is the reaction of the dissolved mass to increase or decrease its concentration due to the dissolution or precipitation of minerals. The main problem associated with the two-step procedure is that it simulates mass transport and reactions independently when in theory these should be handled simultaneously. That is, the amount of mass which is dispersed depends upon the amount of mass which reacts, and vice versa, within the model. Different final concentrations within a mixing cell will occur depending whether mass is dispersed before

what remains is reacted, or if the mass is first reacted and then the remaining mass is dispersed.

This is illustrated by the examples in Table 4.1. In all four cases, the system is represented by a very simple mixing cell model comprised of three cells. The initial concentration of dissolved mass in the cell of interest is 100 units of mass and the two adjacent cells contain no dissolved mass. The dispersion factor and the tolerance are 0.90 and 0.01, respectively. The amount of mass dissolved in a cell at equilibrium following a reaction is 60 units of mass. In the first two cases, the solution is initially oversaturated. When dispersion occurs before reaction, the amount of mass which leaves the cell due to dispersion is 10 units and the amount of mass remaining that precipitates to maintain equilibrium is 30 units. Because the final amount of mass remaining is equal to that at equilibrium (60 units of mass), the solution is saturated. However, if the reaction to maintain equilibrium occurs before dispersion, then the amount of mass which precipitates until equilibrium is reached is now 40 units. Dispersion of the remaining mass (60 units) causes 4 units to leave the cell. Because the final amount of mass in the cell (54 units) is less than that required for equilibrium, the solution is under-saturated. Hence, mass is required to dissolve into solution to once again reach saturation. Thus, depending upon which process is handled first, different amounts of mass precipitating and dispersing will be calculated. Two further examples in Table 4.1, in which the solution is under-saturated, show the same discrepancy between depending upon the order of the calculations. Therefore, a procedure is required to obtain the true initial concentrations of dissolved mass within a cell which satisfies the requirements of both dispersion and reaction.

This problem is solved by iterating between the mass transfer due to dispersion and that due to reactions (Schwartz and Domenico, 1973, Grove and Wood, 1979, Cederberg et al., 1985). Basically this technique involves first, independently adjusting the initial estimates of dissolved mass in a cell by reaction with the geochemical portion of the code. Secondly, the same initial solution is adjusted to account for mass transfer by dispersion.

Table 4.1: Examples of calculating dissolved mass in a cell after the reaction and dispersion of mass without iterating towards a solution.

<u>Case A</u>	<u>Case B</u>
dispersion followed by reaction initial solution is oversaturated	reaction followed by dispersion initial solution is oversaturated
$\chi = 0.9$ $\xi_n = 100.0$ $\xi_d = 90.0 \ (0.9 \times 100.0)$ $\xi_r = 60.0$ amount precipitated: $90.0 - 60.0 = 30.0$ amount dispersed: $100.0 - 90.0 = 10.0$ amount remaining: 60.0 $\therefore$ saturated	$\chi = 0.9$ $\xi_n = 100.0$ $\xi_r = 90.0$ $\xi_d = 60.0 \ (0.9 \times 60.0)$ amount precipitated: $100.0 - 60.0 = 40.0$ amount dispersed: $60.0 - 54.0 = 6.0$ amount remaining: 54.0 $\therefore$ understaturated by 6.0
<u>Case C</u>	<u>Case D</u>
dispersion followed by reaction initial solution is undersaturated	reaction followed by dispersion initial solution is undersaturated
$\chi = 0.9$ $\xi_n = 50.0$ $\xi_d = 45.0 \ (0.9 \times 50.0)$ $\xi_r = 60.0$ amount dissolved: $60.0 - 45.0 = 15.0$ amount dispersed: $50.0 - 45.0 = 5.0$ amount remaining: 60.0 $\therefore$ saturated	$\chi = 0.9$ $\xi_n = 50.0$ $\xi_r = 60.0$ $\xi_d = 54.0 \ (0.9 \times 60.0)$ amount dissolved: $60.0 - 50.0 = 10.0$ amount dispersed: $60.0 - 54.0 = 6.0$ amount remaining: 54.0 $\therefore$ understaturated by 6.0

The two estimates are refined through an iterative procedure of reducing the difference between these two estimates by adjusting the initial solution by this difference. Once the difference is effectively zero, the solution and mass transfer are considered correct. In detail, the procedure undertaken is as follows. New concentrations of all the aqueous components are introduced into each cell by advection by simply moving all mass from an upstream cell into a downstream cell at the beginning of a time step. The new mass introduced into each cell by advection before the system is equilibrated is determined mathematically by:

$$\zeta_n = \zeta_a \quad (39)$$

where: ζ_n = new mass in a cell
 ζ_a = mass introduced into a cell by advection at the start of time step

The amount of mass remaining in a cell after dispersion but before equilibration is adjusted by:

$$\zeta_d = \chi \times \zeta_n \quad (40)$$

where: ζ_d = mass remaining in a cell following dispersion

The amount of mass in a cell due to reactions which transfer mass among the solid and aqueous phases is calculated independently of that determined due to dispersion, and is represented by the following expression:

$$\zeta_r = R(\zeta_n) \quad (41)$$

where: ζ_r = mass in a cell following reactions between the mineral phases
 $R(\zeta_n)$ = reactions which transfer mass between minerals and dissolved components

The difference between the amount of mass in a cell determined with the dispersion expression (equation (40)) and that calculated independently with the reaction expression (equation (41)) is obtained by:

$$\Delta\zeta = \zeta_r - \zeta_d \quad (42)$$

where: $\Delta\zeta$ = difference in mass in a cell due to reactions and dispersion

Mass within the cell is adjusted to obtain a balance between these two processes:

$$\zeta_a = \zeta_d + \Delta\zeta \quad (43)$$

The solution is checked to determine if the difference between the two calculated masses, one due to reactions and another due to dispersion, are within a specified tolerance:

$$|\Delta\zeta| < \text{tolerance} \quad (44)$$

If the change in mass is less than the specified tolerance, then the solution has converged. If the solution has not converged, the procedure starting with equation (40) is repeated until convergence is attained. This procedure is repeated for each stoichiometric component (eg. Na^+ , Ca^{+2} , Cl^- , SO_4^{2-} , etc.) in solution within the system. In most cases, convergence of the system is achieved in approximately 5 iterations. When the entire system has converged, then the amount of mass transferred between the minerals and dissolved components due to geochemical reactions is calculated by:

$$\zeta_{\text{reac}} = \zeta_a - \zeta_d \quad (45)$$

where: ζ_{reac} = mass transfer between solid and aqueous phases

($\zeta_{\text{reac}} > 0 \Rightarrow \zeta_{\text{reac}}$ = amount of mass which precipitates)

($\zeta_{\text{reac}} < 0 \Rightarrow \zeta_{\text{reac}}$ = amount of mass which dissolves)

Mass transfer among mixing cells due to dispersion is calculated as the difference between the adjusted mass in the cell and the mass required to maintain equilibrium:

$$\zeta_{\text{disp}} = \zeta_m - \zeta_r \quad (46)$$

where: ζ_{disp} = mass transfer among mixing cells due to dispersion
 $(\zeta_{\text{disp}} > 0 \Rightarrow \zeta_{\text{disp}} = \text{amount of mass which leaves a cell})$
 $(\zeta_{\text{disp}} < 0 \Rightarrow \zeta_{\text{disp}} = \text{amount of mass which enters a cell})$

The application of an iterative procedure to the determination of the amount of mass that disperses from a cell and either precipitates or dissolves in order to maintain equilibrium between the aqueous and solid phases is illustrated by Table 4.2. The two cases shown by Table 4.2 use the same system as in the example where the calculations were undertaken without iteration. The system consists of three cells, with the cell of interest having an initial concentration of 100 units of mass and the two adjacent cells do not contain mass. The dispersion factor, tolerance for convergence and amount of dissolved mass in a cell at equilibrium, are 0.90, 0.01 and 60 units, respectively. The amounts of mass transfer due to reaction and that leaving a cell due to dispersion, are calculated independently with an iterative technique. For example, in the first case from Table 4.2 (the solution is initially oversaturated), the amount of mass which precipitates due to reaction alone is 40 units (60 units remain in solution) and the amount mass which leaves due to dispersion alone is 10 units (90 units remain in solution). Because the two processes actually occur simultaneously, part of the 40 units of reactive mass loss is actually due to dispersion, and part of the 10 units of dispersive mass loss actually occurs through precipitation. During each iteration, the mass remaining in a cell is adjusted by the difference between that remaining following reaction and dispersion (-30 units). This new value of dissolved mass (70 units) reflects what the actual concentration in the cell should be after mass is removed through reaction alone. The iterative procedure of calculating a

Table 4.2: Examples of calculating dissolved mass in a cell after the reaction and dispersion of mass by iterating towards a convergent solution.

<u>Case A</u> initial solution is oversaturated	<u>Case B</u> initial solution is oversaturated
$\chi = 0.9$ tolerance = 0.1 <i>iteration #1:</i> $\xi_n = 100.0$ $\xi_r = 60.0$ $\xi_d = 90.0 \quad (0.9 \times 100.0)$ $\Delta\xi = -30.0 \quad (60.0 - 90.0)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #2:</i> $\xi_n = 70.0 \quad (100.0 + -30.0)$ $\xi_r = 60.0$ $\xi_d = 63.0 \quad (0.9 \times 70.0)$ $\Delta\xi = -3.0 \quad (60.0 - 63.0)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #3:</i> $\xi_n = 67.0 \quad (70.0 + -3.0)$ $\xi_r = 60.0$ $\xi_d = 60.3 \quad (0.9 \times 67.0)$ $\Delta\xi = -0.3 \quad (60.0 - 0.3)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #4:</i> $\xi_n = 66.7 \quad (67.0 + -0.3)$ $\xi_r = 60.0$ $\xi_d = 60.03 \quad (0.9 \times 66.7)$ $\Delta\xi = -0.03 \quad (60.0 - 60.03)$ $\Delta\xi < \text{tolerance} \quad \therefore \text{stop iterating}$ amount precip.: $100.0 - 66.67 = 33.33$ amount dispersed: $66.67 - 60.00 = 6.67$ amount remaining: 60.0 $\therefore$ solution is saturated	$\chi = 0.9$ tolerance = 0.1 <i>iteration #1:</i> $\xi_n = 50.0$ $\xi_r = 60.0$ $\xi_d = 45.0 \quad (0.9 \times 60.0)$ $\Delta\xi = 15.0 \quad (60.0 - 45.0)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #2:</i> $\xi_n = 65.0 \quad (50.0 + 15.0)$ $\xi_r = 60.0$ $\xi_d = 58.5 \quad (0.9 \times 65.0)$ $\Delta\xi = 1.5 \quad (60.0 - 58.5)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #3:</i> $\xi_n = 66.5 \quad (65.0 + 1.5)$ $\xi_r = 60.0$ $\xi_d = 59.85 \quad (0.9 \times 66.5)$ $\Delta\xi = 0.15 \quad (60.0 - 59.85)$ $\Delta\xi > \text{tolerance} \quad \therefore \text{another iteration}$ <i>iteration #4:</i> $\xi_n = 66.65 \quad (66.5 + 0.15)$ $\xi_r = 60.0$ $\xi_d = 59.985 \quad (0.9 \times 66.65)$ $\Delta\xi = 0.015 \quad (60.0 - 59.985)$ $\Delta\xi < \text{tolerance} \quad \therefore \text{stop iterating}$ amount dissolved: $50.0 - 66.65 = 16.65$ amount dispersed: $66.65 - 60.00 = 6.65$ amount remaining: 60.0 $\therefore$ solution is saturated

difference and adjusting the starting mass in the cell until the initial mass (66.997 units) minus the mass lost due to dispersion (6.991 units) approaches the equilibrium concentration (60 units).

DESCRIPTION OF THE COMPUTER PROGRAMS

This section presents a brief description of the coding of the coupled transport and reaction model. The actual model consists of four computer programs. Each is designed to undertake a specific task related to a simulation and each provides information upon which the next program can continue the simulation process. These four programs are:

STR.FUNC: calculates stream function values at all nodes within a two-dimensional cross section, using the finite element method;

STR.LINE: contours the stream function values to determine the x- and y-coordinates along the stream lines, and calculates the groundwater velocity at each point along the stream line;

STR.TUBE: constructs a series of stream tubes from the stream lines and, given a length of the time step, divides the stream tubes into a series of mixing cells;

MIX.REAC: transport mass by advection and dispersion through a two-dimensional flow regime represented as a series of mixing cells along stream tubes, and simulates geochemical reactions within each cell.

The model is comprised of four programs for several reasons. First, more than one mass transport and reaction scenario may be undertaken with a given set of mixing cells, or a different configuration of mixing cells may be obtained from a given set of flow lines. It is considerably more efficient to build upon the previous calculations than to repeat the entire procedure during each simulation. For example, several different geochemical simulations (program MIX.REAC) may be undertaken with one group of mixing cells generated by program STR.TUBE. Several arrangements of mixing cells may be generated

in STR.TUBE, with a single set of stream lines calculated with STR.LINE. Also, a single set of stream function values calculated within STR.FUNC can be used by STR.LINE to produce several different sets of stream lines. Second, a single code which incorporates all the tasks undertaken by these four programs could encounter limitations in a computer's memory and execution time which would not be encountered when the model is run in four parts. Third, because the model is comprised of separate programs, changes or improvements to each section of the model can be done efficiently and easily without concern for unintentional changes in another part of the program.

The four computer codes are discussed in detail in the remainder of this section. A user's guide containing a list of all input variables and parameters, and the requirements for dimensioning the arrays is presented in Appendix 5. All computer programs, with accompanying example input data sets, printed output and data bases required by MIX-REAC are contained in the diskettes at the end of the thesis.

Program STR.FUNC

The first program is designed to calculate stream function values for a given two-dimensional groundwater flow regime. Data requirements are divided into two groups, grid geometry parameters and hydrogeological variables (Appendix 5). The grid geometry parameters include the length and depth of the flow regime, the number of rows and columns superimposed over the cross section, and the estimated number of nodes and elements comprising the finite element grid. The hydrogeological variables consist of the boundary conditions (constant head or flux nodes), the number and distribution of geological units, the horizontal and vertical hydraulic conductivity and porosity of these units, and the location of the water table.

The basic sequence of operations of the program is illustrated by Figure 7. First, all input data are entered and immediately printed to ensure that the user has correctly entered the data. Next, construction of the nodes and elements which comprise the finite element

grid, assignment of values of hydraulic conductivity and porosity to each element and assignment of the values of boundary conditions to the appropriate nodes, are undertaken automatically within the program. Following the construction of the finite element grid, the distribution of stream function values is determined at all nodes within the flow domain. The finite element technique used in this code is based upon the Galerkin formulation for a steady-state head distribution. This technique is discussed in detail by Pinder and Frind (1972), Pinder and Gray (1977) and Frind and Matanga (1985). The calculation of groundwater velocity and direction of flow within each cell is optional. Calculated values of the stream functions at each node are output to a disk file to be used as input to the second program (STR.LINE). Optional printed output include the nodes and elements comprising the finite element grid, stream function values, the direction of flow and the groundwater velocity field.

Program STR.LINE

Program STR.LINE uses the stream function data generated by STR.FUNC to form stream lines. These stream lines represent the boundaries of the stream tubes through which mass is transported.

The tasks undertaken within this program are illustrated by Figure 8. First, the stream function values, calculated within STR.FUNC, are read from a disk file. Additional data supplied by the user (see Appendix 5) are required to define the values of the stream lines to be generated and to define the grid to which the stream function values are assigned. The x- and y-coordinates of all points along each stream line are determined with a standard contouring package. In order to locate the mixing cells within program STR.TUBE, each boundary of the stream tube requires three closely spaced stream lines. The coordinates are output to a disk file which are in turn used as input for STR.TUBE. Printed output includes an echo of all input parameters and the calculated x- and y-

coordinates. Optional output includes a computer generated plot of the stream lines in a two-dimensional cross section (Figure 5).

Program STR.TUBE

The x- and y-coordinates along the stream lines that are generated by STR.LINE are used by STR.TUBE to form a series of mixing cells along each stream tube. The order of the tasks undertaken by STR.TUBE is illustrated by Figure 9.

The parameters entered by the user to define the mixing cells, listed in Appendix 5, include the number of stream tubes and the size of the time step for mass transport. The coordinates along the stream lines are entered from a disk file which was created by STR.FUNC, with the upper boundary of the flow tube entered first, followed by the coordinates along the lower boundary. Because the lower boundary of the first stream tube forms the upper boundary of the next stream tube, only the coordinates of the lower boundary of this and subsequent stream tubes are entered.

The velocity at each point along the upper stream line is calculated using the procedure described by equations (19) through (22). In order to calculate the groundwater velocities along each boundary of a stream tube, three stream lines are required for each boundary to determine the values of Δx , Δy and $\Delta \Psi$. For example, if the required stream lines boundaries have values of 0.30 and 0.40, then the two sets of stream lines should have values of 0.29, 0.30, 0.31 and 0.39, 0.40, 0.41, respectively (Figure 10). Once these groundwater velocities are determined, the total time required for mass to travel along the entire flow line can be calculated. This procedure is then repeated for the lower boundary of the stream tube. Next, the modified time intervals for mass transport along both stream tube boundaries (equation (25) and (26)) are determined. Based upon these modified time intervals, the x- and y-coordinates defining the corners of the cells are calculated. Two additional points along the stream tube boundaries are calculated in order to more accurately represent the curved shape of the cell boundary (see Figure 4). After the last cell within a

stream tube is processed, the procedure repeated for the next stream tube. However, the values for the upper and lower boundaries of the stream tube need not be recalculated because the lower boundary of a stream tube is also the upper boundary of the next lower stream tube. All values associated with the lower boundary of the previous stream tube are assigned to the corresponding parameters of the upper boundary of the current stream tube. Thus, only the values for the lower boundary must be calculated. Once all the stream tubes are processed, the coordinates of the cell boundaries and the area of the cells are printed.

It should be noted that the number of mixing cells along a flow line is determined by the time step provided by the model user. Thus, an inappropriate time step may lead to the generation of either too many or too few mixing cells along a flow tube, depending upon the total time required for mass to traverse the flow domain. The user is cautioned to check the results of STR.TUBE to ensure that an adequate, but not excessive, number of cells are generated before proceeding to the actual simulation of mass transport and reaction.

Program MIX.REAC

The actual simulations of the transport of mass by advection and dispersion, and the geochemical reactions are undertaken within program MIX.REAC. The portion of the code which simulates the geochemical reactions is a version of *PC-PHREEQEP*, which is converted to a subroutine. Because *PC-PHREEQEP* is essentially the same as the original version of *PHREEQE* (Parkhurst et al., 1980), the reader is referred to this report for a detailed discussion of the theory of the code and the input data. A brief discussion of the input data (including the parameters for *PC-PHREEQEP*) for MIX.REAC is contained within Appendix 5. The following discussion will concentrate upon the programming of the mixing cell theory for mass transport and how this code is coupled with the geochemical code. The operation of subroutine MIX-REAC is illustrated by Figure 11.

Three sets of input are required. The first set of parameters describe the composition of mixing cell model, including the number of cells, size of the time step, area and the x- and y-coordinates along the boundaries of the cells. The second set of data consists of the thermodynamic data bases for aqueous components, minerals and the Pitzer equation parameters. The third group of data is an initial guess of the chemical composition of the solution in each cell, the minerals to be equilibrated in each cell, and the temperature of each cell. Once all the data are entered, the initial solution in each cell are equilibrated with the given minerals to ensure that the starting solutions are chemically and thermodynamically accurate.

Aqueous components are represented with two units of measurements, concentration (as molality) and mass (as grams). Units of concentration are required for the reaction portion of the code because the thermodynamic relationships used in the geochemical code are expressed in terms of concentration. But because only mass, and not concentration, can be transported by advection and dispersion, the aqueous components must also be represented as mass. Throughout the simulation, mass will be converted to concentration and vice versa as required. The conversion is a function of the volume of the cell, density of the solution, porosity and total mass of the aqueous component occupying the cell.

Using the procedure discussed in "Formulation of the Coupled Transport and Reaction Model", mass is advected from each upstream cell and introduced into the next downstream cells at the start of a time step. Advection occurs through all cells simultaneously. The advected mass is not in equilibrium within the given temperature and mineralogical constraints of the new cell and must therefore be adjusted by reaction. At the same time, the mass is being modified by dispersion. The modification of the mass just introduced into a cell by reaction and dispersion occurs cell by cell. The advected mass is adjusted by reaction independently of dispersion because the amount of mass which will react depends upon the amount left after dispersion and vice versa. The difference between

the dispersed and reacted mass is determined and the advected mass is adjusted by this difference through an iterative process until the difference is within a given tolerance. Once the change in the mass within a cell due to reaction has been calculated, the transfer of this mass among the solid and aqueous phases is calculated with the geochemical code. The final chemical characteristics of the solution and mass transferred is printed. This procedure is continued with the following downstream cells until all cells within a stream tube have been processed. Once all the cells have been processed, the entire procedure, starting with the advective transport of mass through the system, continues with the next time step and is repeated until all time steps in the simulation have been processed.

Verification of the Mass Transport Model

The mixing cell model must be verified to ensure that it provides an accurate numerical solution to the advection-dispersion equation. The advective and dispersive transport of mass within the mixing cell model is verified by comparison to an analytical solution to the one-dimensional form of the advection-dispersion equation (equation (1)):

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \quad (47)$$

The analytical solution to equation (47) has been determined by Ogata (1970) using boundary conditions of (1) a homogeneous media, (2) a constant source of mass, and (3) an initial concentration of 0 everywhere:

$$C_{t,i} = C_{0,i} \frac{1}{2} \left(\operatorname{erfc} \left(\frac{s - vt}{2\sqrt{D_L t}} \right) + \exp \left(\frac{sv}{D_L} \right) \cdot \operatorname{erfc} \left(\frac{s + vt}{2\sqrt{D_L t}} \right) \right) \quad (48)$$

where: $C_{t,i}$ = the concentration at a given point along the flow path
 $C_{0,i}$ = the concentration at the source ($s = 0$)
 s = distance along a flow path at which concentration is calculated
 t = time elapsed since the introduction of mass into the flow regime

The dispersion coefficient describes the mechanical mixing of a solute as a function of the characteristics of the porous media (known as dispersivity) and the movement of the fluid. Dispersivity is scale-dependent, with values in natural groundwater flow systems ranging up to 100 m (Freeze and Cherry, 1979). The dispersion coefficient is expressed as (Schwartz, 1977):

$$D_L = \epsilon_L v \quad (49)$$

where: ϵ_L = longitudinal dispersivity
 v = groundwater velocity

Rather than express concentration in absolute terms, it is typically expressed as a relative concentration defined as the ratio of $C_{t,i}$ to $C_{0,i}$. The plot of this concentration ratio along the flow path, at specific times, is commonly known as a breakthrough curve (Figure 12).

Because the velocity field in the flow regime dictated by the analytical solution of Ogata (1970) is constant, we have defined a constant cell size, and hence a constant transit time (Δt), for all cells comprising the mixing cell model.

Verification focuses upon how well the calculations from the mixing cell model can reproduce the results from the analytical solution. Three sets of simulations, with three comparisons in each set, were undertaken. The parameters used in the mixing-cell model, including groundwater velocity (v), length of the cells (Δl), the total length of the system and the dispersivity (and hence the dispersion coefficient; D_L) were varied among the simulations. The values of the time step and the number of cells remain constant through all simulations and are set to 100 years and 100 cells, respectively. In each case, the length of the mixing cell is calculated from given values of Δt and v . The dispersion coefficient used in the analytical solution is calculated with equation (31) from the known values of Δt , v , Δl

and the lumped parameter dispersion factor (χ). Three values of χ chosen for study are 0.1, 0.5 and 0.9, representing mass loss through dispersion of 10%, 50% and 90%, respectively. The parameters used by both the mixing-cell model and the analytical solution during the sensitivity analyses are summarized by Table 4.3. Values calculated by both the analytical solution and the mixing cell model are plotted at times of 1000, 3000, 5000 and 7000 years. The actual units of time (e.g. seconds, days, years) is not critical to the validity of the model because, with all parameters having consistent units, the calculations are essentially dimensionless. For example, rather than use a time step in terms of years, a time step of thousands of years could be used as long as the other hydrogeological and transport parameters are referenced to this larger scale of time.

The results of the verification simulations are presented by Figures 12a through 12i. Generally, the mixing cell model reproduces the calculations from the analytical solution very well. The ratio between the size of the cells and the groundwater velocity did not affect the accuracy of the solution. However, the value of the dispersive factor ($\hat{\chi}$) affected the accuracy of the results of the mixing cell model. Mass is transferred further along the flow system through an increasing number of cells during each time step as the dispersion factor decreases. As shown by Figures 12c, 12f and 12i, where $\hat{\chi} = 0.1$, the solution from the mixing cell model diverges from the analytical solution where the slope of the breakthrough curve changes rapidly. During a simulation, this divergence increases as the elapsed time (i.e. number of calculations) increases. The divergence of the mixing cell solutions is due to numerical error caused by repeated calculations with the mixing cell model. Because each calculation is not exact but is subject to roundoff error, the accuracy of each successive calculation is reduced slightly. With a large value of the dispersion factor (i.e. small values of the dispersion coefficient) and with a reasonable number of time steps, the two solutions match very well. Hence, the accuracy of the calculations can be increased by reducing the number of time steps rather than by reducing the size of the time step.

Table 4.3: Parameters used in the verification simulations.

scenario:	A	B	C
v	0.01 m/yr	0.10 m/yr	1.00 m/yr
Δt	100 yr	100 yr	100 yr
Δl	1 m	10 m	100 m
max. cell length	100 m	1000 m	10000 m
number of cells	100	100	100
ϵ : simulation 1	0.05 ¹ (Fig. 11a)	0.50 ² (Fig. 11d)	5.00 ³ (Fig. 11g)
ϵ : simulation 2	0.25 ¹ (Fig. 11b)	2.50 ² (Fig. 11e)	25.00 ³ (Fig. 11h)
ϵ : simulation 3	0.45 ¹ (Fig. 11c)	4.50 ² (Fig. 11f)	45.00 ³ (Fig. 11i)
$\hat{\chi}$: simulation 1	0.9 (Fig. 11a)	0.9 (Fig. 11d)	0.9 (Fig. 11g)
$\hat{\chi}$: simulation 2	0.5 (Fig. 11b)	0.5 (Fig. 11e)	0.5 (Fig. 11h)
$\hat{\chi}$: simulation 3	0.1 (Fig. 11c)	0.1 (Fig. 11f)	0.1 (Fig. 11i)

1: dispersivity at a laboratory scale

2: dispersivity of a small groundwater flow system

3: dispersivity of a basin-scale groundwater flow system

Stability of the Mass Transport Solution

Most numerical models for mass transport which are based on the finite difference or finite element methods incur some numerical dispersion or numerical error. This error is due to the loss precision when the calculations are preformed by a computer which represents numbers with a finite number of digits. Two values, known as Peclet and Courant numbers, are used to describe the stability of a numerical solution to the advection-dispersion equation in terms of the grid spacing (Δx , Δy) and the size of the time step (Δt). The Courant and Peclet numbers are defined as:

$$C = \frac{v_i \cdot \Delta t}{\Delta l_i} \quad (50)$$

$$P = \frac{v_i \cdot \Delta l_i}{D_j} \quad (51)$$

where: **C** = Courant number
P = Peclet number
 v_i = average linear groundwater velocity ($i = x, y$)
 Δl_i = grid spacing ($i = x, y$)
 D_j = dispersion coefficient ($j = L, T$)

Because the Courant number is a ratio of the distance mass travels by advective transport during a time step to the size of the grid, it relates the stability of the numerical solution to the advective transport parameters. The Peclet number similarly relates the stability of the numerical solution to dispersive transport. If this error is small, numerical dispersion is analogous to physical dispersion, because numerical dispersion is proportional to the groundwater velocity term (Miller and Benson, 1983). However, by choosing either too large of a time step, too few time steps, an incorrect grid spacing, or an incorrect number of cells, the error will reach a point where instability problems with the solution will occur. The criteria for a stable numerical solution, described by de Marsily (1986) and Daus and Frind (1985) is:

$$C \leq 1 \quad (52)$$

$$P \leq 2 \quad (53)$$

Substituting equation (50) into equation (52), and equations (49) and (53) into equation (51), respectively gives:

$$v_i \cdot \Delta t \leq \Delta l_i \quad (54)$$

$$\frac{D_L}{v_i} \leq \frac{\Delta l_i}{2} \quad (55)$$

Equations (54) and (55) essentially imply that advective transport should not be greater than the distance represented by the grid spacing during a single time step and that dispersive transport should not be less than half of the grid spacing during a single time step for a stable solution. The lumped parameter advection term (equation (30)) and the lumped parameter dispersion terms (equations (31) and (32)) are essentially Courant and Peclet numbers, respectively.

The instability problems expressed by the Courant number for the lumped parameter model have been eliminated by using a computer code to obtain the optimum values of cell size and location within a two-dimensional groundwater flow regime, based on the calculated groundwater velocity field and a specified time step for mass transport. As previously discussed, the size of the cells (Δl) is determined by the stream tube computer code which generates the cells given a value of Δt . Thus, mass will not be transported by advection by more than one cell during a single time step.

The criteria for choosing a value of the dispersive factor can not be based upon the relationship between the Peclet number (equation (51)) and the lumped parameter dispersion delay term (equation (31)) because these two terms refer to the distance that mass moves and the amount of mass which is transferred, respectively.

To determine whether the solution is stable (i.e. it does not exhibit oscillations and it convergence), a series of simulations were undertaken to test the stability and sensitivity of various model parameters for predicting an accurate solution. Parameters that remain constant during all simulations include the length of the system (10,000m) and the groundwater velocity (0.10 m/yr). Solutions are shown at times of 1,000, 3,000 and 5,000 years. The only parameter to vary during these analyses is the lumped parameter dispersive factor ($\hat{\lambda}$), which varies from 0.01 (essentially all mass is dispersed from a cell) to 0.99 (essentially no dispersion occurs). The values of the mixing cell parameters for the three simulations are listed in Table 4.4.

Results of the analyses (Figure 13) show that the mixing cell model is stable during all five simulations. The stability of the solution to a wide range of values of $\hat{\lambda}$ is expected because the lumped parameter dispersive factor controls the amount of mass transferred and not the distance dispersed. As mass is moved from an upstream cell to a downstream cell, more will become available to be dispersed to subsequent downstream cells. Hence as $\hat{\lambda}$ decreases, mass is spread throughout an increasingly larger portion of the flow system as time progresses. Therefore, it appears that the mixing cell model will not be subject to numerical instability as long as (1) the model determines the number of cells and the size of these cells, based on a predefined value of the time step, and (2) the value of $\hat{\lambda}$ is between 0 and 1.

While the Peclet number (equation (51)) aids the user of the distributed parameter models, a similar guide does not exist for lumped parameter models. However, an examination of Figure 11 shows that as the lumped parameter dispersive factor decreases, the solution calculated by the mixing cell model diverges from that determined with the analytical solution. This divergence is generally negligible when $\hat{\lambda}$ is greater than 0.5. Thus, the solution will be more accurate if $\hat{\lambda}$ is greater than 0.5.

Table 4.4: Parameters used in the sensitivity analyses simulations.

simulation:	1	2	3	4	5
v	0.10 m/yr	0.10 m/yr	0.10 m/yr	0.10 m/yr	0.10 m/yr
Δt	1000 yr	1000 yr	1000 yr	1000 yr	1000 yr
Δx	100 m	100 m	100 m	100 m	100 m
number of cells	100	100	100	100	100
$\hat{\chi}$	0.01	0.10	0.50	0.90	0.99

APPLICATION OF THE TRANSPORT AND REACTION MODEL

A major emphasis of this thesis is to develop a numerical model capable of simulating mass transport and geochemical reactions in deep sedimentary basins rather than to undertake a detailed quantitative analysis. The goal of the simulations presented in this section is to demonstrate the applicability of the model. Simulations are undertaken within a framework of sensitivity analyses. Sensitivity analyses involve the systematic variation of one or more parameters while the rest are held constant. The parameters chosen for study are not extensive, but are sufficient to demonstrate the types of parameters which can be studied by the model. A complete analysis of the parameters and processes influencing diagenesis in deep sedimentary basins would require a multitude of simulations to focus upon the variety of minerals, solution chemistries and salinities, pH, temperature, groundwater velocity and other parameters. To demonstrate the applicability of the code, we have chosen an analysis of a simple yet important geological system, the carbonate system. Simulations focus upon how the formation or dissolution of minerals in sedimentary basins respond to various hydrogeological and chemical stresses. This work is intended to provide insight into which parameters influence mineral stability from a theoretical point of view. Because we are more interested in understanding processes rather than investigating an actual site, the simulations are hypothetical to the extent that they do not represent an actual sedimentary basin. However, the values assigned to the hydrogeological, mineralogical and geochemical parameters are typical of those found in a variety of clastic sedimentary basins.

The first stage of the modelling procedure involves the application of program STR.FUNC to the calculation of stream function values in a two-dimensional cross section. The region chosen for this analysis consists of a single homogeneous geological unit, with both a horizontal and vertical hydraulic conductivity of 10^{-6} cm/s and a porosity of 0.05, which are typical of sandstone. The water table has a linear slope.

The flow domain is discretized to form a regular rectangular grid of 25 columns and 10 rows, with a horizontal and a vertical node spacing of 500m and 100m, respectively. Constant flux values are assigned to all nodes along the water table. The other three boundaries are no flow boundaries, defined by assigning a constant stream function value of 0.0 to each node along the side and lower boundary.

The stream function values calculated with program STR.FUNC are contoured and shown by Figure 5a. In order to form a series of mixing cells for the transport and reaction of mass, one stream tube is chosen for detailed analysis. This stream tube has upper and lower stream line boundaries with values of 0.25 and 0.30, respectively. The other two stream lines required to accompany the each boundary stream line for the calculation of the groundwater velocity, and hence the boundaries of the mixing cells, have values of 0.24 and 0.26, and 0.29 and 0.30 for the upper and lower boundaries, respectively (Figure 10). The coordinates along the stream tube boundaries, generated by STR.LINE, are used by STR.TUBE to form the mixing cells. With a time step for mass transport of 200,000 years, twenty mixing cells are formed. The large time step was chosen because with such a large time interval it can be assumed that the aqueous components and solid phases will attain equilibrium. Although twenty cells are formed, program MIX.REAC only uses the first ten cells because we are interested in mass transport and reactions within a recharging groundwater flow system. The remaining ten cells follow groundwater discharge from the point of deepest penetration of the flow system. All upcoming scenarios are run with the same mixing cell configuration.

The minerals used to demonstrate mass transfer between solids and the groundwater are calcite and dolomite. Except as noted, all scenarios have a constant value of the dispersive factor, partial pressure of CO_2 , temperatures ranging from 25°C to 200°C, and salinities ranging from approximately a m_{NaCl} of 0.15 to m_{NaCl} of 3.50. A dispersive factor of 0.9 indicates that 10% of dissolved mass is transferred from a mixing cell during each time step. The ranges of temperature and salinity are typical of those occurring in deep

sedimentary basins. Four parameters chosen for study are designed to study chemical, physical and hydrogeological parameters influencing the stability of minerals. These parameters are:

1. salinity of the solution
2. temperature
3. dispersion
4. partial pressure of CO_2

Scenario 1: Salinity of the solution

Salinity is a dominant chemical characteristic of groundwater in deep sedimentary basins. The salinity of some brines may be extremely high. Two analyses were undertaken to investigate how the salinity of brines can affect the solubility of minerals. In both cases, the salinity is controlled by the partial dissolution of halite which causes ionic strength to be proportional to the molality of Na^+ . The first simulation was run at a constant ionic strength of approximately 1.0 to provide a basis from which to compare results obtained in a system with higher salinity. The second case represents a system in which the ionic strength varies from approximately 0.15 to 3.5.

The results of mass transfer of calcite and dolomite between solid and aqueous phases, and the chemical composition of the solutions, are listed in Table 4.5. The concentration of both Ca^{+2} , Mg^{+2} and CO_3^{2-} increase as the salinity of the solution increases. The increase in the concentration of these ions is expected because more ion interactions occur as the solution becomes more saline. Hence more dissolution of minerals is required in order to increase the concentration of the free ions required to maintain equilibrium with the solid phases. However, a maximum concentration is attained at an ionic strength of approximately 1.5 to 2.0. This trend has also been noted by Harvie et al. (1984). The transfer of mass between dissolved constituents and solid phases is increased as the salinity of the solution increases. Because more mass is available to be either dispersed from cells

Table 4.5: Chemistry of the solutions and amount of mass transferred between aqueous and solid phases due to changes in salinity and temperature.

solution with constant salinity and variable temperature:

Temp.	I	pH	m_{Ca}^1	m_{Mg}^1	$m_{calcite}^2$	$m_{dolomite}^2$
50°C	1.00	6.99	0.326×10^{-2}	0.135×10^{-2}	-0.490×10^{-4}	$+0.302 \times 10^{-4}$
75°C	1.01	6.90	0.294×10^{-2}	0.662×10^{-3}	-0.245×10^{-4}	$+0.176 \times 10^{-4}$
100°C	1.00	6.84	0.249×10^{-2}	0.293×10^{-3}	-0.119×10^{-4}	$+0.104 \times 10^{-4}$
125°C	0.98	6.83	0.202×10^{-2}	0.117×10^{-3}	-0.359×10^{-5}	$+0.550 \times 10^{-5}$
150°C	0.95	6.85	0.158×10^{-2}	0.427×10^{-4}	$+0.708 \times 10^{-5}$	$+0.250 \times 10^{-5}$
175°C	0.91	6.89	0.122×10^{-2}	0.143×10^{-4}	$+0.119 \times 10^{-5}$	$+0.127 \times 10^{-5}$
185°C	0.90	6.91	0.110×10^{-2}	0.906×10^{-5}	$+0.565 \times 10^{-6}$	$+0.103 \times 10^{-6}$

solution with variable salinity and constant temperature:

Temp.	I	pH	m_{Ca}^1	m_{Mg}^1	$m_{calcite}^2$	$m_{dolomite}^2$
50°C	0.55	6.99	0.236×10^{-2}	0.129×10^{-2}	-0.491×10^{-5}	-0.849×10^{-5}
50°C	1.26	6.98	0.298×10^{-2}	0.136×10^{-2}	-0.978×10^{-5}	-0.675×10^{-5}
50°C	1.94	6.96	0.334×10^{-2}	0.130×10^{-2}	-0.463×10^{-5}	-0.227×10^{-6}
50°C	2.38	6.95	0.340×10^{-2}	0.124×10^{-2}	-0.134×10^{-5}	$+0.128 \times 10^{-5}$
50°C	2.62	6.94	0.337×10^{-2}	0.120×10^{-2}	-0.310×10^{-6}	$+0.155 \times 10^{-5}$
50°C	3.02	6.92	0.334×10^{-2}	0.114×10^{-2}	-0.230×10^{-6}	$+0.216 \times 10^{-5}$
50°C	3.16	6.91	0.328×10^{-2}	0.112×10^{-2}	$+0.125 \times 10^{-6}$	$+0.701 \times 10^{-5}$

solution with variable salinity and temperature:

Temp.	I	pH	m_{Ca}^1	m_{Mg}^1	$m_{calcite}^2$	$m_{dolomite}^2$
50°C	0.55	7.32	0.204×10^{-2}	0.884×10^{-3}	-0.490×10^{-4}	$+0.631 \times 10^{-5}$
75°C	1.26	7.22	0.208×10^{-2}	0.459×10^{-3}	-0.214×10^{-4}	$+0.927 \times 10^{-5}$
100°C	1.96	7.16	0.190×10^{-2}	0.207×10^{-3}	-0.912×10^{-5}	$+0.712 \times 10^{-5}$
125°C	2.43	7.14	0.168×10^{-2}	0.870×10^{-4}	-0.263×10^{-5}	$+0.364 \times 10^{-5}$
150°C	2.71	7.15	0.148×10^{-2}	0.342×10^{-4}	$+0.456 \times 10^{-5}$	$+0.168 \times 10^{-5}$
175°C	3.22	7.19	0.140×10^{-2}	0.126×10^{-4}	$+0.357 \times 10^{-5}$	$+0.956 \times 10^{-6}$
185°C	3.43	7.22	0.140×10^{-2}	0.821×10^{-5}	$+0.136 \times 10^{-5}$	$+0.736 \times 10^{-7}$

1: equilibrium concentrations of Ca^{+2} and Mg^{+2} .

2: molality of calcite and dolomite transferred between aqueous and solid phases
(+ve = precipitation; -ve = dissolution).

with high concentration to cells with low concentration, more mass will either dissolved into or precipitated from the solution, respectively. This effect of dispersion will be discussed in detail in a following scenario.

Scenario 2: Temperature

Large variations in temperatures occur with depth in sedimentary basins. In this analysis, the effect of temperatures on the solubility of calcite and dolomite in diagenetic environments (25°C to 200°C) is examined. A simulation was conducted using an NaCl solution with a constant ionic strength of approximately 1.0 over temperatures ranging from 25°C to 200°C. The ionic strength of the solution is set to 1.0 in order to remove the effects of ionic strength on mineral solubility.

The effect of temperature on the solubility of calcite is shown by Table 4.5. As temperature increases in a brine, the amount of Ca^{+2} , Mg^{+2} and CO_3^{2-} all decrease. The mass transfer of calcite and dolomite also decreases due to less mass being transferred due to advection or dispersion into a cell. The simulation also shows that there is a decrease in the concentration of Ca^{+2} of approximately 25% for every 25°C increase in temperature. The large decrease in dissolved mass implies less mass is available for transfer between aqueous and solid phases. Thus, temperature is an important parameter controlling the stability of calcite.

Scenario 3: Dispersion

Dispersion is an important hydrogeological parameter controlling the physical transport of dissolved mass within a groundwater flow regime. Because this process spreads and mixes mass, it has the effect of transferring mass from a region of high concentration to a region of low concentration. The simulations discussed here illustrate the effect of a decreasing dispersive factor ($\chi = 0.90, 0.80, 0.60$), which results in an

increasing amount of mass being transferred among the mixing cells (i.e. 10%, 20% and 40% of mass is transferred, respectively).

Results of these three simulations are listed in Table 4.6. As the dispersive factor increases, the amount of Ca^{+2} transferred among the cells increases and the amount of calcite and dolomite reacted increases. Because mass is dispersed from a cell with a relatively high concentration to one with a lower concentration, calcite or dolomite in the former cell must be dissolved. Dissolution occurs in order to supply the necessary amount of dissolved mass to both maintain equilibrium within the cell and to provide mass to an adjacent cell with a lower concentration. The cell with a lower concentration accepting this mass will become oversaturated upon receiving the dispersed mass. Hence mass must be transferred to a solid phase by precipitation in order to both accept the addition influx of Ca^{+2} and to maintain equilibrium with calcite and dolomite. The increase in the amount of mass precipitated or dissolved due to a 10% increase in dispersion among cells is relatively small, typical in the order of 1% of the total Ca^{+2} in the system. Thus, while it is apparent that dispersion affects the solubility of calcite and dolomite, its importance is minor relative to other process or parameters.

Scenario 4: P_{CO_2}

This scenario is designed to demonstrate how calcite and dolomite are affected by changes to the partial pressure of dissolved CO_2 within a brine. The analyses use three different values of P_{CO_2} , which are; -2.5, -2.0 and -1.5. All three values are typical of those found in subsurface environments (Freeze and Cherry, 1979).

The changes in the solution and the mass transfer of calcite are listed in Table 4.7. In all cases, as expected, the concentration of Ca^{+2} increases as P_{CO_2} increases. However, in all three cases, the concentration of Ca^{+2} increases to a maximum at an ionic strength of approximately 1.5, after which it decreases as salinity continues to increase. Harvie et al. (1984) also reported similar results. The pH of the solution decreases in order to balance

Table 4.6: Chemistry of the solutions and amount of mass transferred between aqueous and solid phases due to changes in dispersion.

Temp	I	pH	equilibrium conc. ¹		molality of calcite transferred ²		
			m _{Ca}	m _{Mg}	$\chi = 0.9$	$\chi = 0.8$	$\chi = 0.6$
50°C	0.55	7.32	0.204×10^{-2}	0.885×10^{-3}	$-.267 \times 10^{-4}$	$-.571 \times 10^{-4}$	$-.129 \times 10^{-3}$
75°C	1.26	7.22	0.208×10^{-2}	0.459×10^{-3}	$-.214 \times 10^{-4}$	$-.466 \times 10^{-4}$	$-.114 \times 10^{-3}$
100°C	1.96	7.16	0.190×10^{-2}	0.207×10^{-3}	$-.912 \times 10^{-5}$	$-.209 \times 10^{-4}$	$-.509 \times 10^{-4}$
125°C	2.43	7.14	0.168×10^{-2}	0.870×10^{-4}	$-.263 \times 10^{-5}$	$-.657 \times 10^{-5}$	$-.214 \times 10^{-4}$
150°C	2.71	7.15	0.148×10^{-2}	0.342×10^{-4}	$+.456 \times 10^{-5}$	$+.971 \times 10^{-5}$	$+.213 \times 10^{-4}$
175°C	3.22	7.19	0.140×10^{-2}	0.126×10^{-4}	$+.357 \times 10^{-5}$	$+.805 \times 10^{-5}$	$+.218 \times 10^{-4}$
185°C	3.43	7.22	0.140×10^{-2}	0.821×10^{-5}	$+.136 \times 10^{-5}$	$+.351 \times 10^{-5}$	$+.123 \times 10^{-4}$

1: equilibrium concentrations of Ca^{+2} and Mg^{+2} are the same for all three values of χ .

2: +ve = precipitation; -ve = dissolution.

Table 4.7: Chemistry of the solutions and amount of mass transferred between aqueous and solid phases due to changes in P_{CO_2} .

Temp	I	$P_{CO_2} = -2.5$		$P_{CO_2} = -2.0$		$P_{CO_2} = -1.5$	
		m_{Ca}^1	$m_{calcite}^2$	m_{Ca}^1	$m_{calcite}^2$	m_{Ca}^1	$m_{calcite}^2$
50°C	0.55	$.141 \times 10^{-2}$	$-.181 \times 10^{-4}$	$.204 \times 10^{-2}$	$-.267 \times 10^{-4}$	$.298 \times 10^{-2}$	$-.392 \times 10^{-4}$
75°C	1.26	$.144 \times 10^{-2}$	$-.146 \times 10^{-4}$	$.208 \times 10^{-2}$	$-.214 \times 10^{-4}$	$.303 \times 10^{-2}$	$-.312 \times 10^{-4}$
100°C	1.96	$.133 \times 10^{-2}$	$-.643 \times 10^{-5}$	$.190 \times 10^{-2}$	$-.912 \times 10^{-5}$	$.276 \times 10^{-2}$	$-.139 \times 10^{-4}$
125°C	2.43	$.118 \times 10^{-2}$	$-.139 \times 10^{-5}$	$.168 \times 10^{-2}$	$-.263 \times 10^{-5}$	$.243 \times 10^{-2}$	$-.411 \times 10^{-5}$
150°C	2.71	$.107 \times 10^{-2}$	$+.439 \times 10^{-5}$	$.148 \times 10^{-2}$	$+.456 \times 10^{-5}$	$.213 \times 10^{-2}$	$+.568 \times 10^{-5}$
175°C	3.22	$.105 \times 10^{-2}$	$+.155 \times 10^{-5}$	$.140 \times 10^{-2}$	$+.357 \times 10^{-5}$	$.198 \times 10^{-2}$	$+.469 \times 10^{-5}$
185°C	3.43	$.108 \times 10^{-2}$	$+.250 \times 10^{-6}$	$.140 \times 10^{-2}$	$+.136 \times 10^{-5}$	$.196 \times 10^{-2}$	$+.103 \times 10^{-6}$

1: equilibrium concentrations of Ca^{+2} .

2: molality of calcite transferred between phases +ve = precipitation; -ve = dissolution.

the effects of increasing CO_3^{2-} . The transfer of mass between aqueous and solid phases increases as P_{CO_2} increases because, as noted above, more dissolved mass is available to disperse from or to cells having relatively higher and lower concentrations, respectively. Thus, the increased concentrations result in more mass being dissolved from, or precipitated to solid phases in the cells with higher and lower concentrations of dissolved mass, respectively. There is an increase of approximately 30% in the concentration of Ca^{+2} with an increase of P_{CO_2} of 0.5. The change in the mass transfer also increase, but is considerably greater (approximately 90%). Thus, P_{CO_2} is an extremely important and sensitive parameter affecting the solution chemistry and mass transfer within this system.

CONCLUSIONS

The chemical character of groundwater and the stability of minerals in deep sedimentary basins are primarily influenced by two processes; transport of dissolved mass and reaction. The transport of aqueous constituents through a groundwater flow regime is controlled by advection and dispersion. The transfer of mass from one phase to another, including between aqueous and solid phases, is controlled by chemical reactions.

The numerical solution of mass transport with reaction in a two-dimensional heterogeneous media, and with multiple dissolved constituents, is a complex task. Limitations of present methods relate to (1) the accuracy of the numerical techniques used to solve for transport and reaction, (2) the complexity of the physical system which can be represented, (3) the variety of aqueous components which can be described, and (4) the limits on the computer capabilities. These problems generally are due to the difficulty of numerically combining the partial differential equations which describe mass transport (advection and dispersion) with the algebraic equations which define the reactions.

A numerical model has been developed which will simulate the transport of mass by advection and dispersion and subject the dissolved constituents to chemical reactions. The model is based upon a lumped parameter - mixing cell procedure which is used to simulate

the advective transport and dispersion of dissolved mass. Lumped parameter models do not consider the spatial variability and heterogeneities which occur in natural systems. Hence, they are not as theoretically rigorous as conventional numerical techniques such as the finite difference or finite element methods. However, simplifications to the physical system within a limited spatial and temporal averaged context are generally accepted in numerical modelling. Thus, the lumped parameter - mixing cell approach presents an attractive alternative to conventional modelling methods.

The model developed here is an extension of current lumped parameter theory. It is based upon a multi-cell approach in which a series of mixing cells are generated within a stream tube. Because the cells are located within a stream tube, all mass introduced into the first cell and transported through the system by advection will be confined to the stream tube. The lateral boundaries of the cells are located at intervals corresponding to the distance through which mass will travel through the stream tube due to advection during a predefined interval of time. Thus, at the start of each time step, all mass within a cell will be transported to the next cell by advection. Dispersion is incorporated into the model to spread and mix the dissolved mass among the cells. The cells are generated within a computer program based upon the location of the stream tube within the flow regime and a given time step for mass transport. Typical problems with numerical stability commonly associated with the improper location, size and number of cells, the number and size of the time steps for transport, and as well a groundwater velocity, direction of flow and the value used for dispersion, are essentially eliminated. The transport portion of the code has been verified by comparison of the numerical results to the solution of an analytical equation.

The reaction portion of the model is handled by coupling a geochemical code to the mixing cell model. The numerical technique employed to couple the transport and reaction models is performed with a two-step approach, in which the physical processes transporting the mass are solved independently of the chemical processes which transfer mass between solid and aqueous phases. A two-step procedure is necessary to determine

the correct concentrations of dissolved components in each mixing cell to balance the requirements of mass transfer among aqueous components and solid phases, and mass transfer among cells due to dispersion.

Although the goal of this thesis is the development of a mass transport and reaction code, and not a quantitative study of the parameters influencing diagenesis, a brief demonstration of the applicability of the code was included here. Through the use of sensitivity analyses, a brief study of some geochemical, hydrogeological and physical parameters which affect the stability of carbonate minerals in a diagenetic environment containing brines was undertaken. To undertake a complete analysis of the parameters and processes influencing mineral stability in diagenetic environments would require a multitude of simulations. However, the simulations presented here indicate that the two most important parameters controlling the stability of calcite and dolomite are the partial pressure of CO_2 and the temperature of the system. The effects of the salinity of the solution and dispersion contribute significantly less to mass transfer. More importantly, these analyses have succeeded in illustrating the validity and usefulness of this technique.

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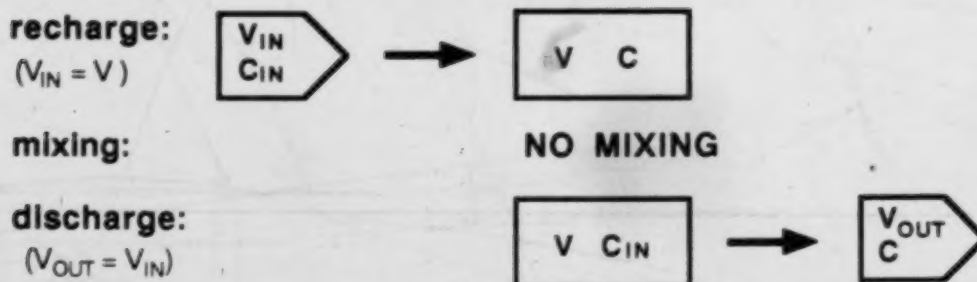
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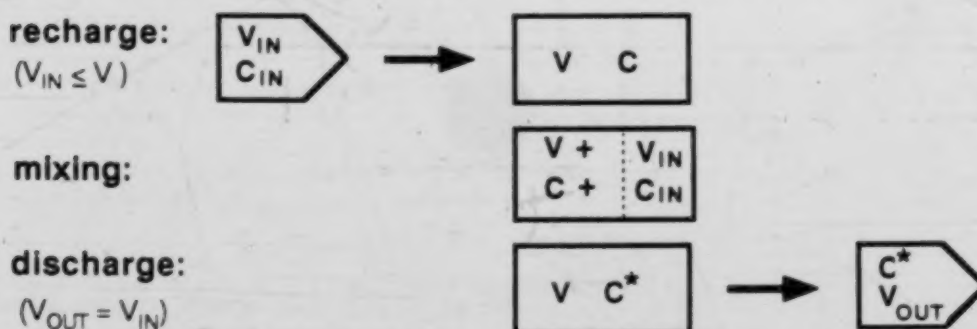
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(a) PISTON FLOW MODEL



(b) WELL MIXED MODEL



(c) MODIFIED MIXING CELL MODEL

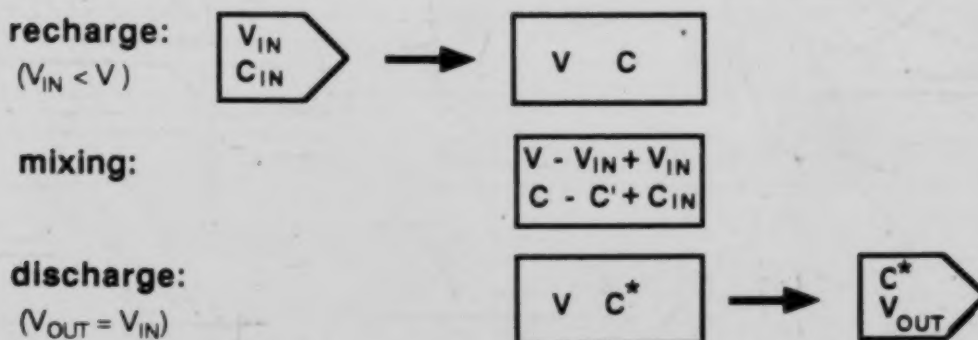


Figure 1. Schematic illustration of the flow, mixing and discharge processes within a mixing cell.

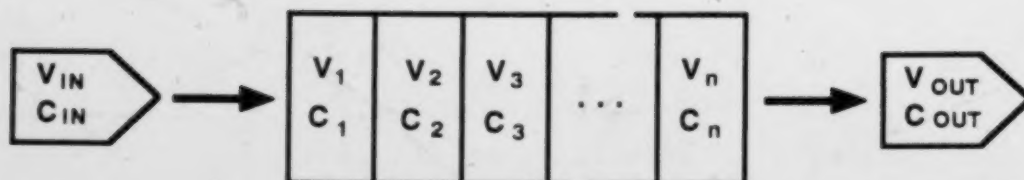


Figure 2. The discrete-state compartmental mixing cell model.

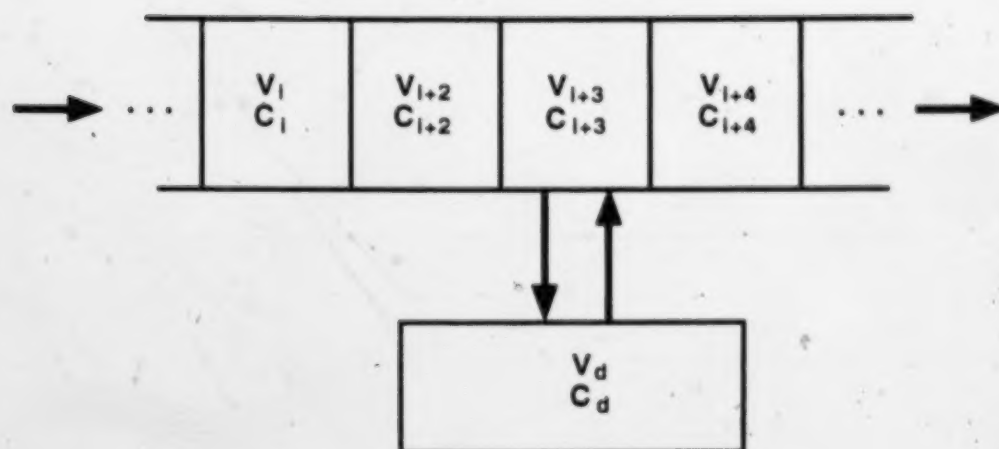


Figure 3. Illustration of the relationship of a dead-cell to a discrete-state compartmental mixing cell model.

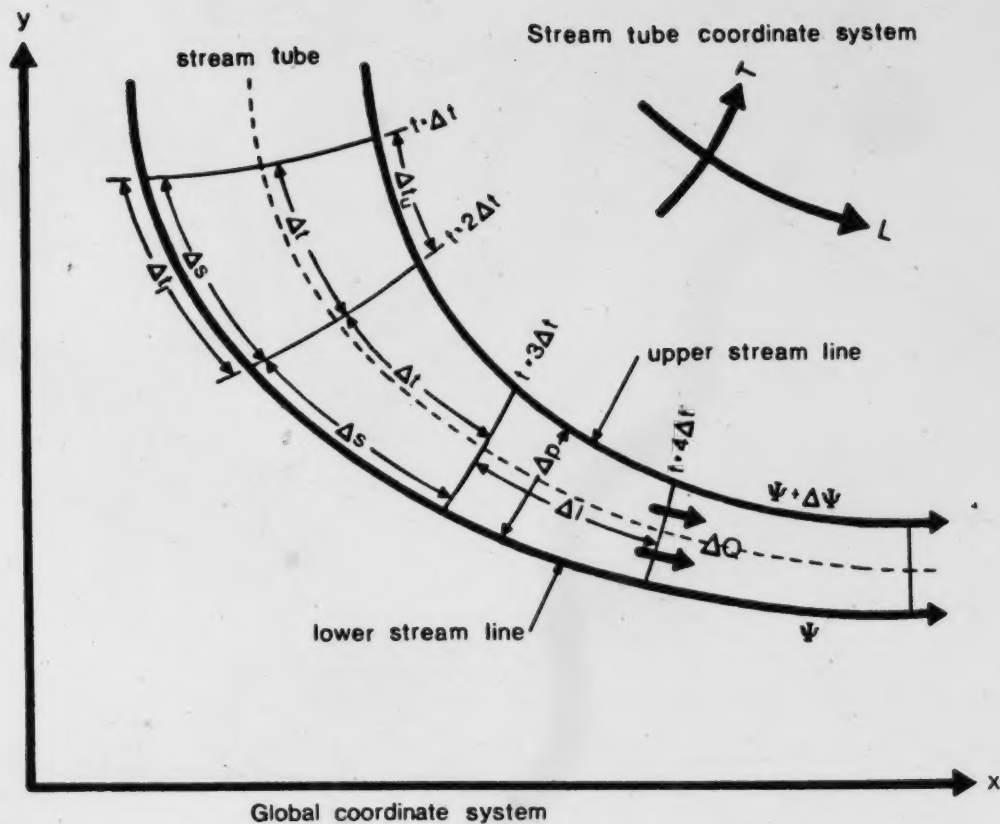
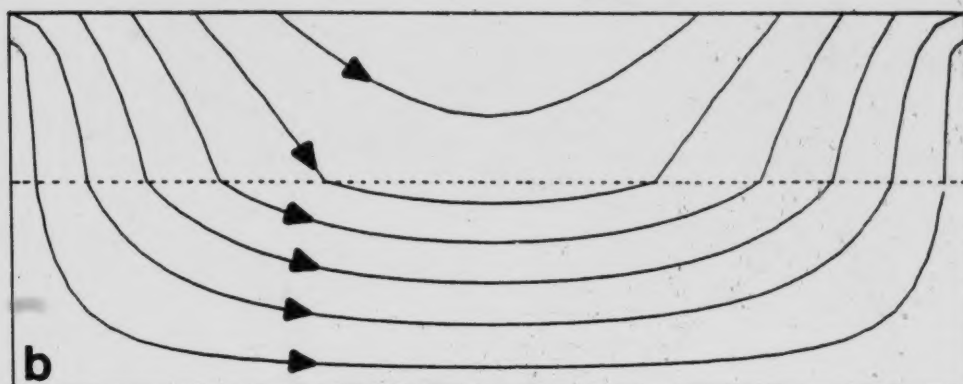
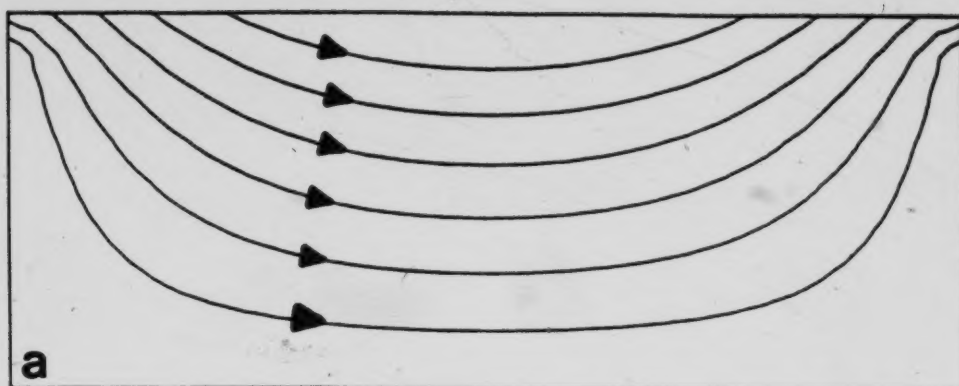
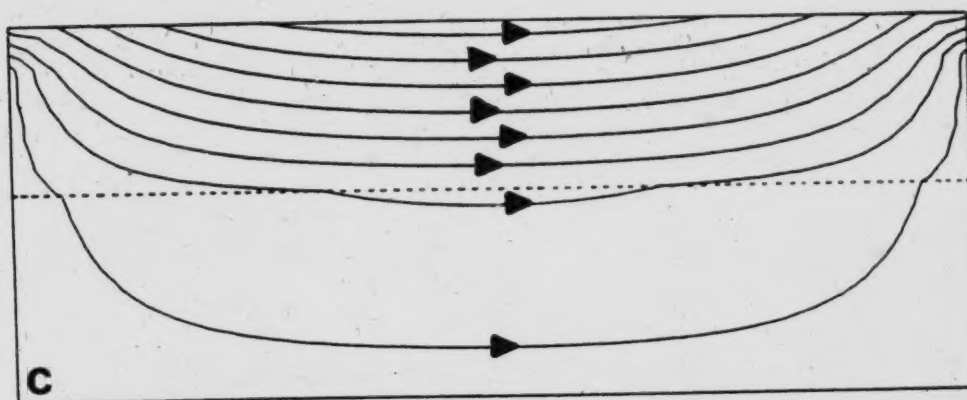


Figure 4. Schematic illustration of the parameters used to describe flow within a stream tube to define the variables within a stream tube model.



$K(\text{upper}) < K(\text{lower})$



$K(\text{upper}) > K(\text{lower})$

Figure 5. Examples of stream lines and flow tubes calculated by the model for a homogeneous and layered geological systems.

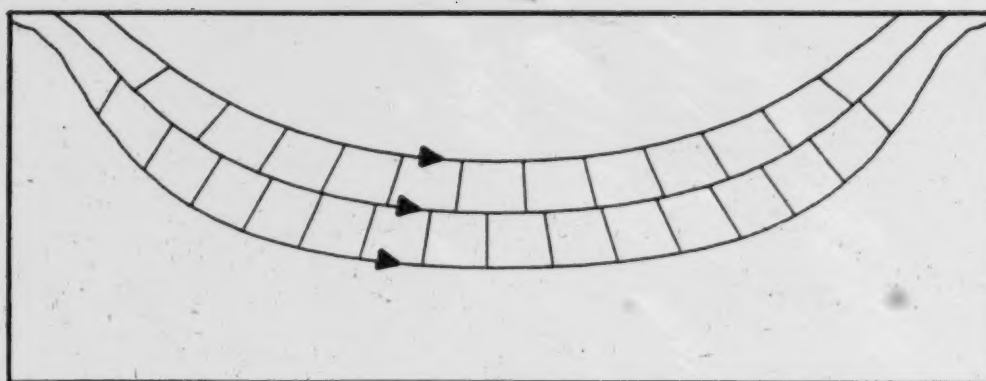


Figure 6. A two-dimensional flow region subdivided into a series of mixing cells.

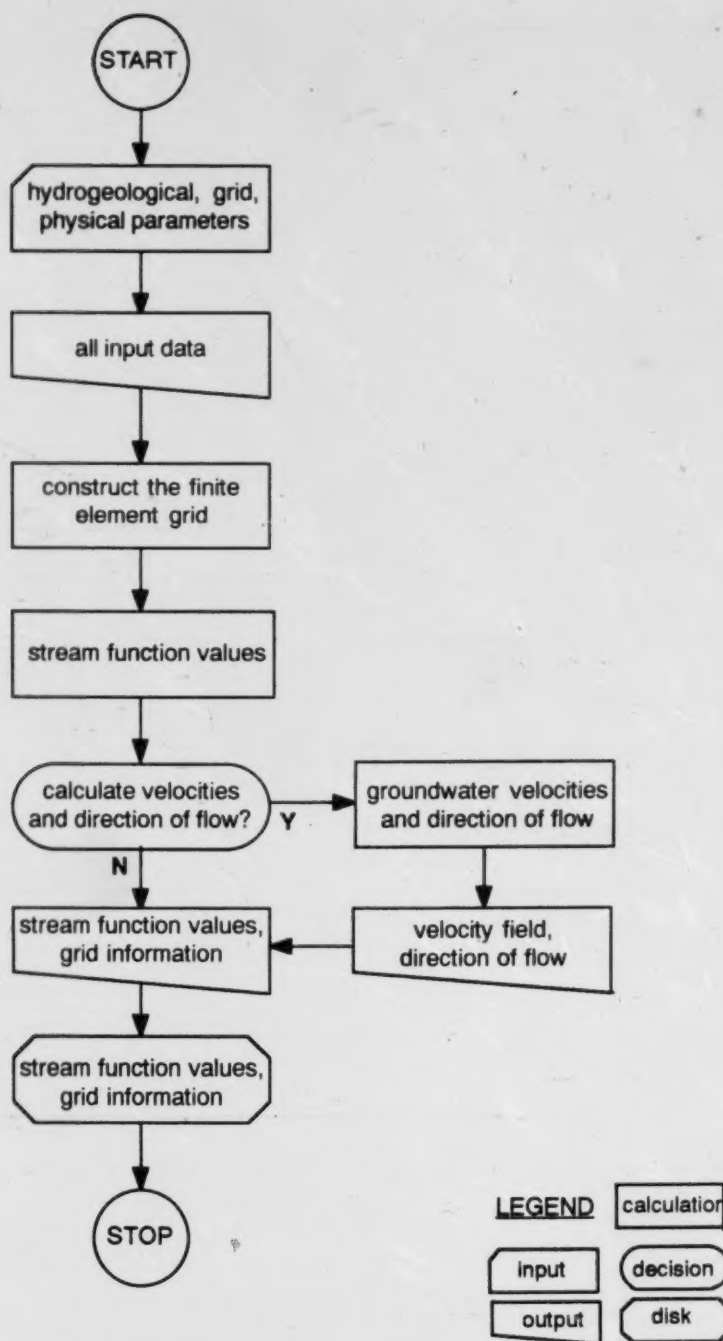


Figure 7. Flow chart for program STR.FUNC.

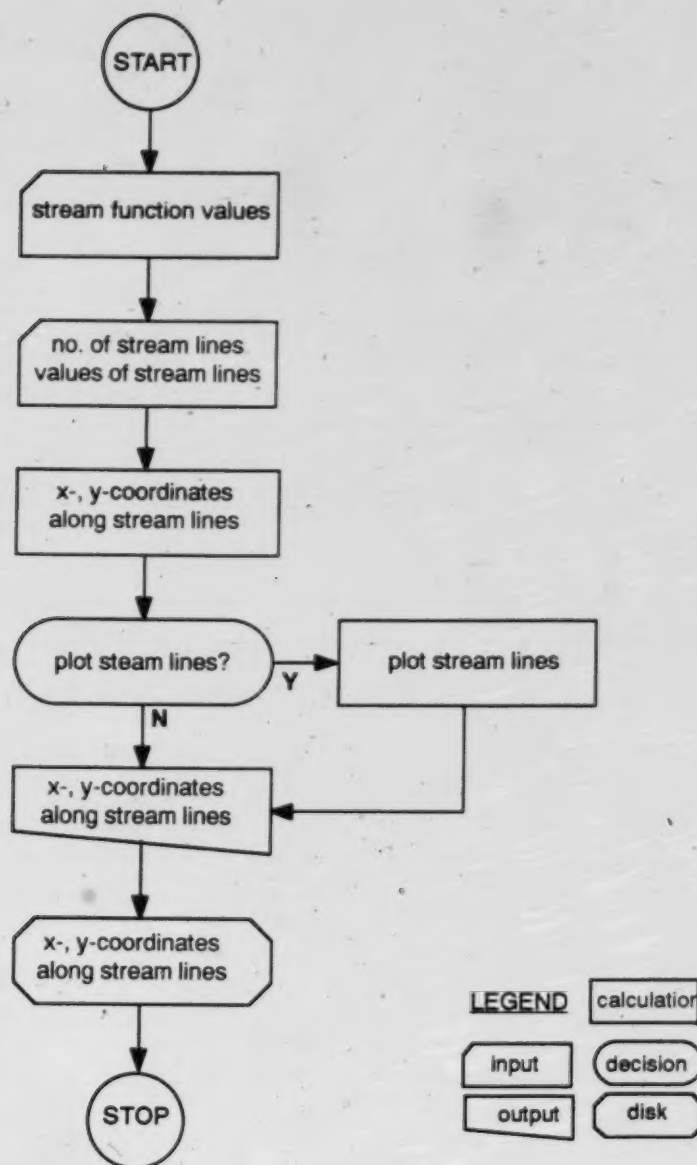


Figure 8. Flow chart for program STR.LINE

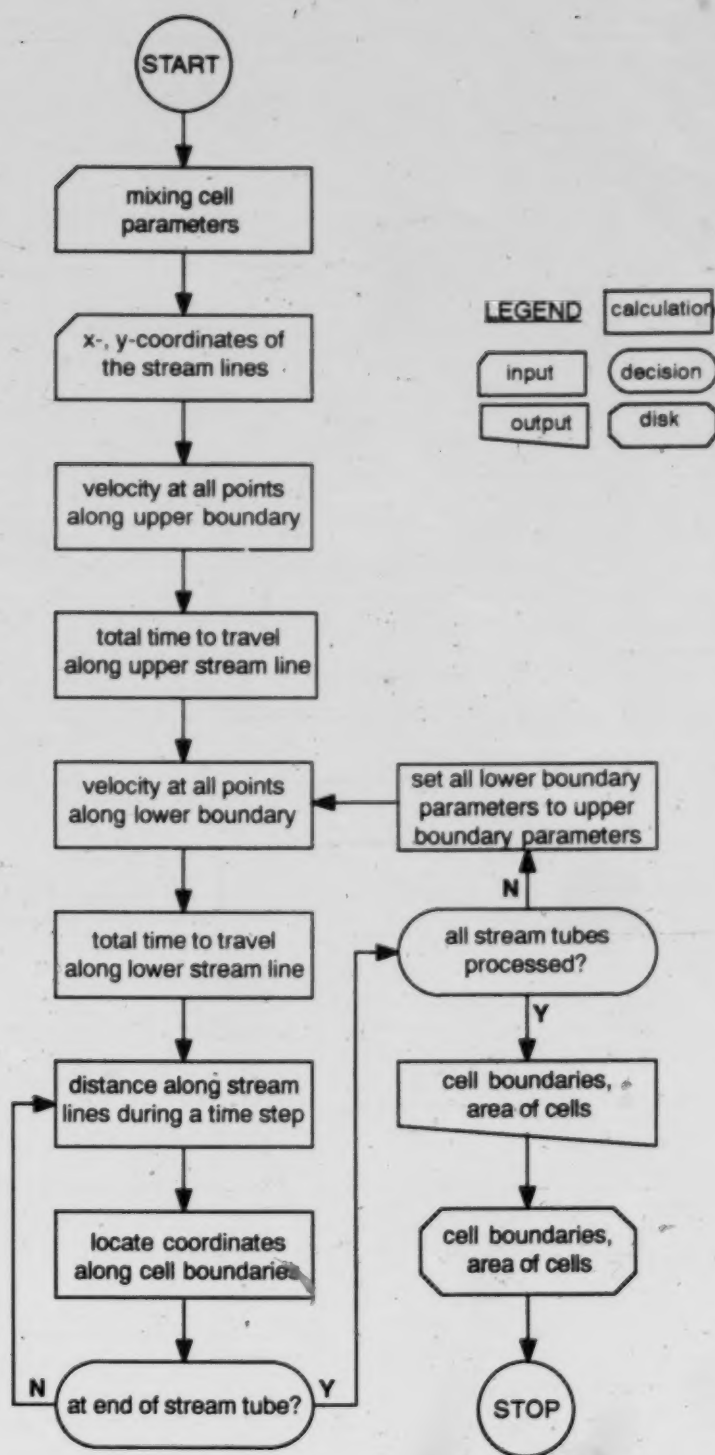


Figure 9. Flow chart for program STR.TUBE.

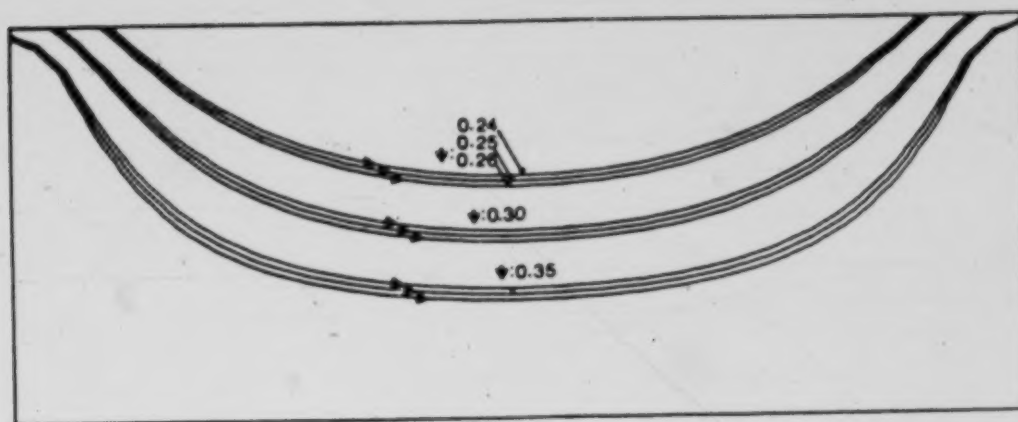


Figure 10. Illustration of two stream lines along the boundaries of the stream tube which are used to calculate the groundwater velocity.

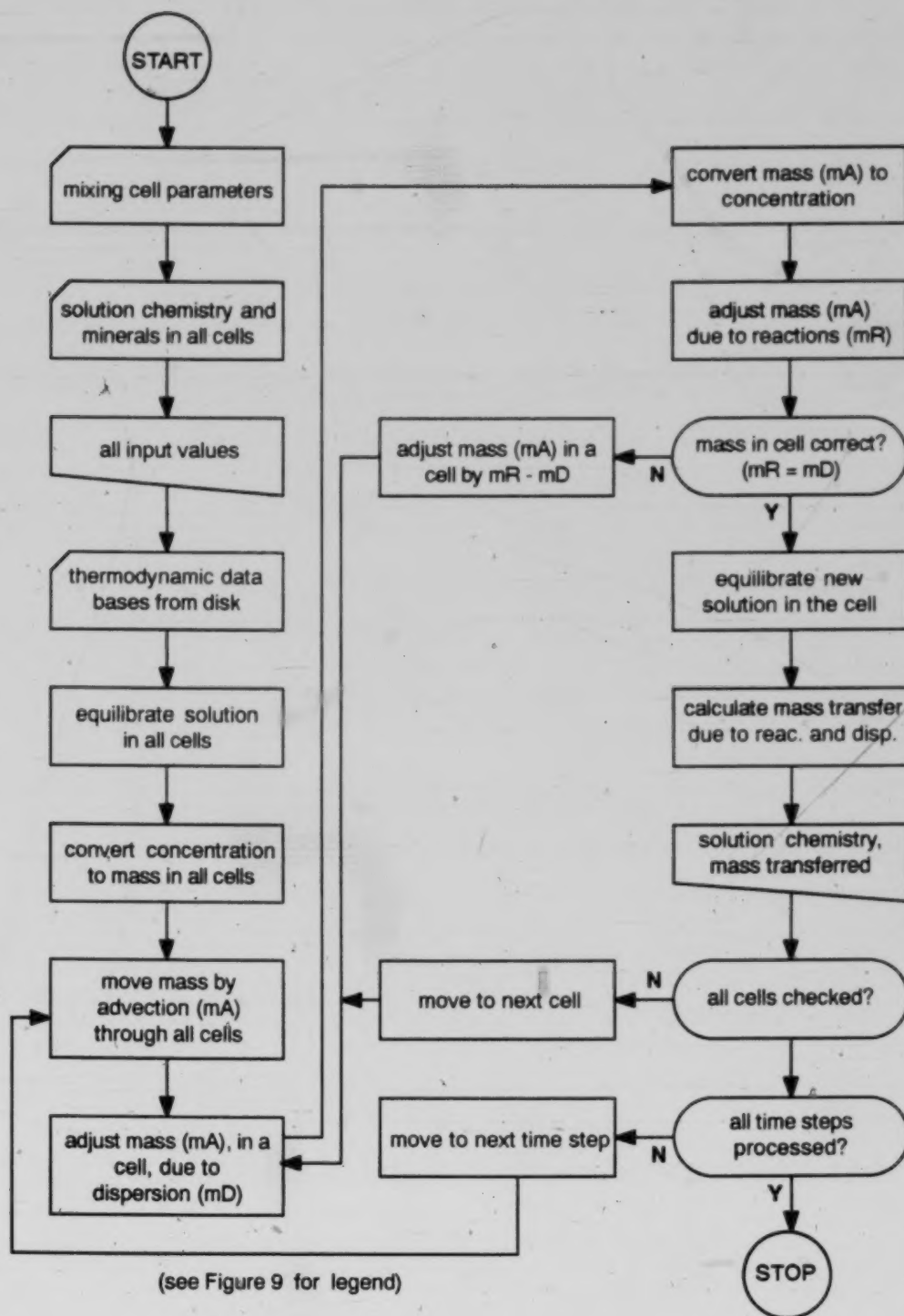


Figure 11. Flow chart for program MIX.REAC.

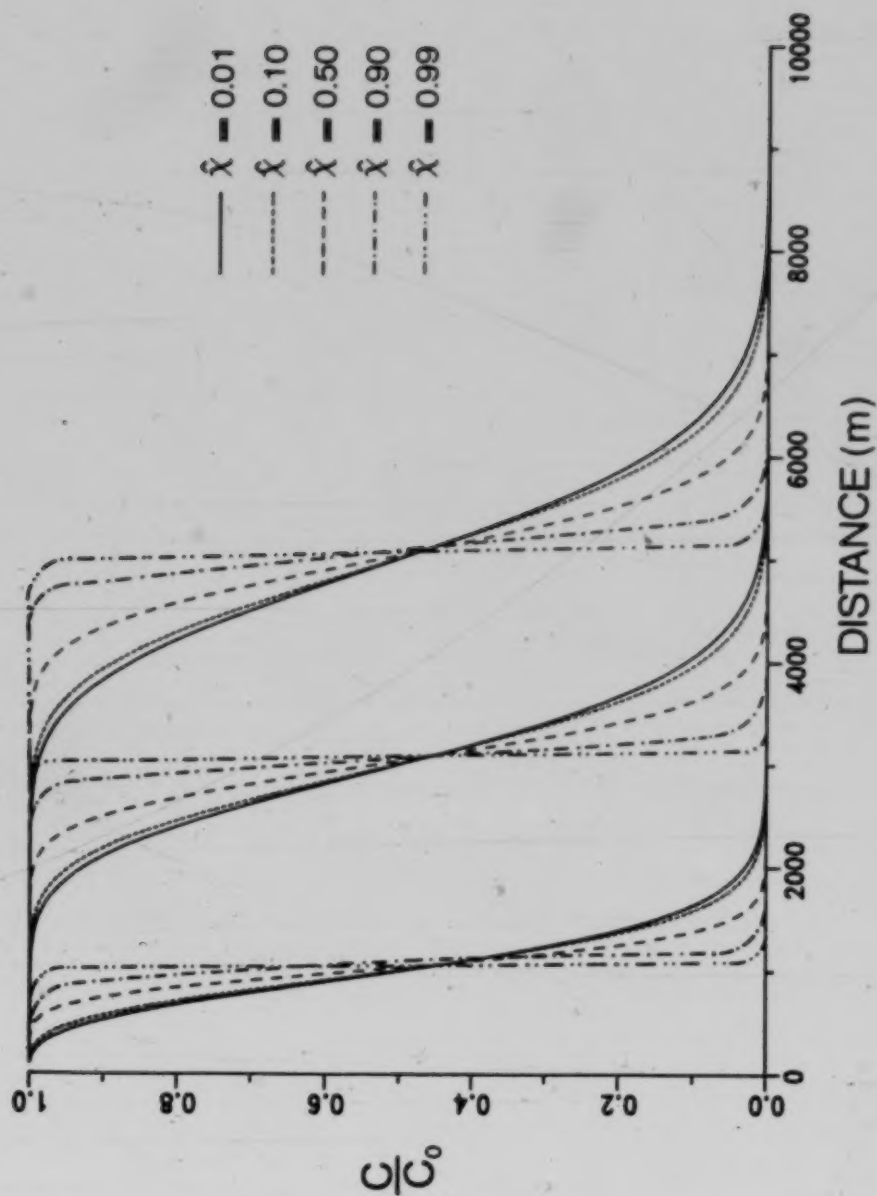


Figure 12. Stability of the mixing-cell code as a function of the lumped dispersive delay parameter.

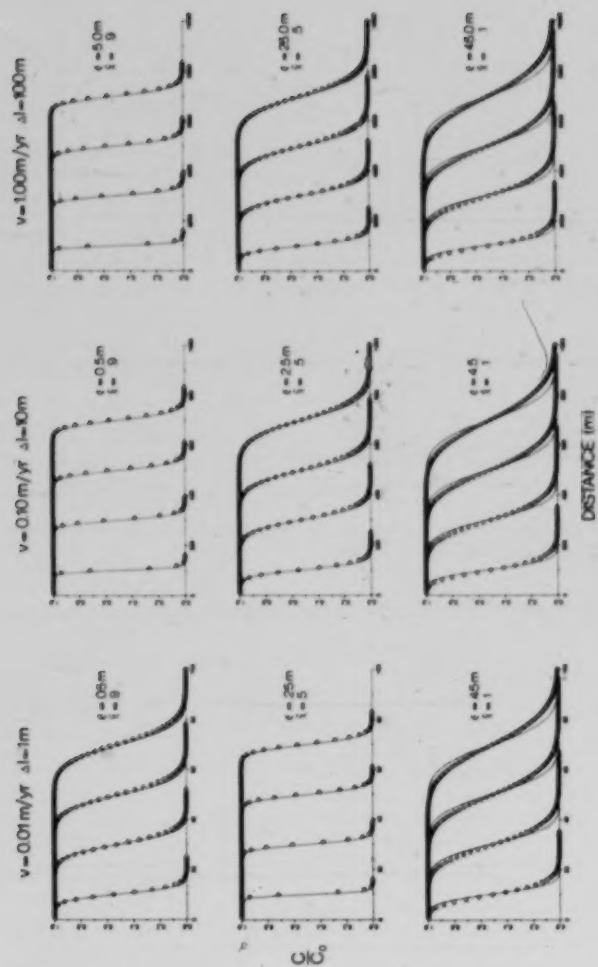


Figure 11 Verification of the advective-dispersive portion of the code. Comparison between the analytical solution of Ogata (1970) (solid line) with the mixing cell model (symbols) at 1000, 3000, 5000 and 7000 years.

V. CONCLUSIONS AND RECOMMENDATIONS

Quantitative techniques currently in use are inappropriate for application to studies of mineral solubility in deep sedimentary basins because they are limited in their ability to (1) study minerals dissociation and precipitation reactions in brines, (2) accurately account for the effects of temperatures of up to 200°C on the aqueous components, and (3) consider the effects of the physical transport processes of advection and dispersion along with geochemical reactions. This thesis has addressed these problems through the development of a numerical model that can simulate the transport of dissolved mass through a deep sedimentary basin and react it with the confining rock. The research has focused upon the development of the code rather than its application to studies of diagenesis.

In order to study the effects of both the transport and reaction processes in a hydrogeological environment, two different models were developed and ultimately coupled. These models are a geochemical code used to react the mass and a transport code which simulates the movement the mass through the flow regime.

A geochemical model and accompanying data base of thermodynamic parameters for the aqueous components and minerals is required to describe precipitation and dissolution of minerals, mass transfer among dissolved and solid phases, and the chemistry of the solution within a variety of geological systems. While several existing geochemical codes meet these requirements, they are generally inappropriate for hydrogeological environments in which the chemistry of the water is a brine and temperatures reach 200°C. These codes are typically limited to a maximum salinity of approximately 6000 mg/L because of the portion of the code which calculates the activity coefficients of ions. Current geochemical modelling codes use a Debye-Hückel based equation to calculate an activity coefficient. However, the theory upon which these equations is based is invalid at high salinities and hence, the calculated mineral solubilities are inaccurate. Another major limitations of these codes relates to the data base of thermodynamic parameters for aqueous

species. Because considerable ion interaction occurs in brines, an extremely large number of different complexes exist. The solubility of a mineral in a brine, as calculated by a geochemical code, is dependent upon the type of aqueous species which are included within the data base of thermodynamic parameters. Thermodynamic data for some of the species necessary to characterize a solution may not be included in the data base or if present, the data may not be accurate. Typically, fewer and less accurate data exist for high temperatures.

This research has reduced these limitations through the modification of an existing geochemical modelling code, known as *PHREEQE*. Specific improvements to the geochemical code include:

1. A specific ion interaction model for calculating stoichiometric activity coefficients in very saline solutions, called the Pitzer equations, has been incorporated into *PHREEQE*. This model accounts for the effects of ion pairing and the electrostatic charges that occurs to a solution as salinity increases. Hence, this enables the code to accurately predict the distribution of mass among the various phases.
2. Because stoichiometric activity coefficients are calculated using the Pitzer equations, rather than activity coefficients for individual ions, the data base only requires the stoichiometric components comprising the aqueous system, and need not contain most ion pairs.
3. A comprehensive data base of equilibrium constants for the mineral dissociation reactions, thermodynamic parameters for the aqueous components, and the ion interaction parameters for the Pitzer equations has been compiled for the major constituents and minerals found in sedimentary basins. All values can be interpolated between 0°C and 200°C.
3. While considerable data for the ion interaction parameters required by the Pitzer equations are available at 25°C, little data are available for other temperatures.

That which is available is typically published in a variety of forms. A model has been developed for estimating the missing ion interaction parameters required by the Pitzer equations at both 25°C and from 0°C to 200°C.

4. The improved version of *PHREEQE* has been optimized to run on an I.B.M. personal computer. This modification increases the versatility of the code and decreases the costs of simulations.

The mass transport code accounts for both physical transport processes, advection and dispersion. While a number of such computer programs are available, few have been coupled to an extensive geochemical reaction code. It is difficult to numerically combine the partial differential equations that describe transport with the algebraic equations that define reactions. The limitations encountered when applying deterministic techniques, such as the finite element or finite difference methods, to complex scenarios are due to the physical limits of (1) the computer memory requirements for a large grid, (2) memory requirements for a variety of aqueous species and minerals, and (3) the limitations of execution time required to solve the large problems.

These restrictions have been overcome in this thesis by adopting a lumped parameter - mixing cell approach to the transport of mass. Conventional mixing cell models do not consider the spatial variability and heterogeneities which occur in a natural system and the handling of mass transport is not as theoretically rigorous as the distributed parameter models. Our lumped parameter model represents a significant improvement over the current models because:

1. The lumped parameter model is comprised of several mixing cells, each with its own physical, hydrogeological and chemical properties. Thus, while lumping of parameters still occurs, it is not as restrictive as conventional single cell models. Also, as the number of cells increases, the mixing cell model acquires properties of a distributed parameter model.

2. The cells in our model are formed within stream tubes that are derived with a finite element model. By placing the cells within a stream tube, the advective transport of mass is restricted by the bounding flow lines to a smaller but better defined region of the flow system. Instead of solving for the transport, distribution and geochemical reactions of mass with the thousands of elements or cells which comprise a finite element or finite difference grid, our model requires calculations in only a few tens of cells. A considerable saving in computer costs results, which can be translated into more complex scenarios for the same cost.
3. The lateral boundaries of the mixing cells are located at intervals of the distance traveled during advective transport during a time step. Hence, during each time step, all mass in one cell is transport into the next downstream cell. This procedure effectively removes the necessity of solving the partial differential equations for advective transport.
4. The location, size and number of cells within the flow system are determined numerically within the code, based on the hydrogeological properties of the stream tube, the velocity of the groundwater (both calculated within the code) and the size of the time step for mass transport (supplied by the user). Hence, the stability and convergence problems typically associated with most transport codes is essentially eliminated. Also, a dispersive factor which accounts for mass transport by dispersion is supplied by the user. The model then determines how much mass and how far it will disperse without creating stability problems.
5. The coupled processes of transport and reactions utilize a two-step approach, in which the calculation of mass transfer among the phases due to geochemical reactions is solved independently of the calculation for mass transfer among cells due to dispersion. This not only simplifies the mathematics of the problem without significant loss in accuracy, but it also provides a direct solution to the amount of mass transferred through the system due to reactions and dispersion.

6. The reaction portion of the code is an improved version of the proven geochemical code *PHREEQE*. This allows simulations within a variety of complex geological systems.

Because this thesis represents a broadly based study concentrating upon the vital concepts necessary to build a successful model, some important areas have not been pursued to the depth to which they warrant. Areas for future research and limitations of the present code are discussed here. The limitations and areas of future research focus primarily upon the geochemical portion of the code:

1. Considerable data are available for the ion interaction parameters required by the Pitzer equations for the major components in natural waters (alkali elements, alkali earth elements, Cl^- , SO_4^{2-}) at 25°C . However, little data are available for many geologically important elements which are present in trace quantities. This problem is especially prevalent at high temperatures. Experimental data should be obtained and refined against mineral solubility calculations.
2. Many ion pairs form in solutions as a result of changes in pH or redox potential rather than changes in salinity. These elements include acids (e.g. H_2SO_4^0 , HSO_4^- , SO_4^{2-}), hydrolysed metals (e.g. $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{+2}$, Al^{+3}), and redox species (e.g. Fe^{+2} , Fe^{+3}). The entire pH distribution of these species must be included in a data base if the geochemical system has large variations in pH and pe. However, few of these data are available. This is an area of considerable geological importance which has been essentially neglected.
3. While a model for predicting high temperature values of the ion interaction parameters for the Pitzer equations has been present in this thesis, it is largely unvalidated against a large group of mineral solubility data. Mineral solubility measurements from the published literature, at high temperatures, should be obtained and the proposed regression model refined and extensively verified using these data.

4. The thermodynamic data for clays are quite limited even though these minerals are important phases in sedimentary basins. Both theoretical and experimental studies are required to quantify the equilibrium constant for formation and dissolution reactions over a wide range of temperatures.
5. Recent research is beginning to examine the effects of pressure on the ion interaction parameters required by the Pitzer equations. The influence of pressure on the Pitzer parameters should be included in this model.
6. More model studies should be conducted to thoroughly examine the effect of various geochemical, hydrogeological and physical parameters upon the formation and stability of minerals in diagenetic environments.

This study has only been a first attempt to develop a practical mass transport and geochemical reaction code. The results obtained in this thesis indicate that the concepts are viable and that further development of both the geochemical code and its data base are warranted.

APPENDIX 1**ION INTERACTION PARAMETERS FOR THE PITZER EQUATIONS**

Table A.1: Species in the data base of ion interaction parameters

cation		anion		neutral species	
no.	ion	no.	ion	no.	ion
1	Na ⁺	1	Cl ⁻	1	CO ₂ ⁰
2	K ⁺	2	SO ₄ ⁻²	2	CaCO ₃ ⁰
3	Ca ⁺²	3	HSO ₄ ⁻	3	MgCO ₃ ⁰
4	Mg ⁺²	4	CO ₃ ⁻²		
5	MgOH ⁺	5	HCO ₃ ⁻		
6	H ⁺	6	OH ⁻		
7	Mn ⁺²	7	Br ⁻		
8	Fe ⁺²	8	I ⁻		
9	Sr ⁺²	9	Al(OH) ₄ ⁻		
10	Ba ⁺²				
11	Li ⁺				
12	Al ⁺³				
13	Al(OH) ⁺²				
14	Al(OH) ₂ ⁺				

Table A.2: Ion interaction parameters: $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and C_{ca}^{∞} at 25°C.

cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{∞}	max m	reference
Na ⁺	Cl ⁻	0.07650	0.26640	0.0	0.001270	6.0	2,11,8
Na ⁺	SO ₄ ²⁻	0.01958	1.11300	0.0	0.004970	4.0	2,19
Na ⁺	HSO ₄ ⁻	0.04540	0.39800	0.0	0.0		2
Na ⁺	CO ₃ ²⁻	0.03620	1.51000	0.0	0.005200	1.0	8,9
Na ⁺	HCO ₃ ⁻	0.02800	0.04400	0.0	0.0	1.0	8,9
Na ⁺	OH ⁻	0.08640	0.25300	0.0	0.004400	6.0	2,11,8
Na ⁺	Br ⁻	0.09730	0.27910	0.0	0.001160	4.0	11
Na ⁺	I ⁻	0.11950	0.34390	0.0	0.001800	3.5	11
Na ⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
K ⁺	Cl ⁻	0.04835	0.21220	0.0	-0.000840	4.8	2,11
K ⁺	SO ₄ ²⁻	0.04995	0.77930	0.0	0.0	5.5	2,11
K ⁺	HSO ₄ ⁻	-0.00030	0.17350	0.0	0.0		2
K ⁺	CO ₃ ²⁻	0.14880	1.43000	0.0	-0.001500		2
K ⁺	HCO ₃ ⁻	0.02960	-0.01300	0.0	-0.008000		2
K ⁺	OH ⁻	0.12980	0.32000	0.0	0.004100	5.5	2,11
K ⁺	Br ⁻	0.05690	0.22120	0.0	-0.001800	5.5	11
K ⁺	I ⁻	0.07460	0.25170	0.0	-0.004140	4.5	11
K ⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
Ca ²⁺	Cl ⁻	0.31590	1.61400	0.0	-0.000340	2.5	2,11
Ca ²⁺	SO ₄ ²⁻	0.20000	3.19730	-54.240	0.0		2
Ca ²⁺	HSO ₄ ⁻	0.21450	2.53000	0.0	0.0		2
Ca ²⁺	CO ₃ ²⁻	0.0	0.0	0.0	0.0		2
Ca ²⁺	HCO ₃ ⁻	0.40000	2.97700	0.0	0.0		2
Ca ²⁺	OH ⁻	-0.17470	-0.23030	-5.720	0.0		2
Ca ²⁺	Br ⁻	0.38160	1.61325	0.0	-0.000339	3.0	11
Ca ²⁺	I ⁻	0.43793	1.80675	0.0	-0.000838	2.0	11
Ca ²⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
Mg ²⁺	Cl ⁻	0.35235	1.68150	0.0	0.005190		2
Mg ²⁺	SO ₄ ²⁻	0.22100	3.34300	-37.230	0.025000	3.0	2,11
Mg ²⁺	HSO ₄ ⁻	0.47460	1.72900	0.0	0.0		2
Mg ²⁺	CO ₃ ²⁻	0.0	0.0	0.0	0.0		2
Mg ²⁺	HCO ₃ ⁻	0.32900	0.60720	0.0	0.0		2
Mg ²⁺	OH ⁻	0.0	0.0	0.0	0.0		2
Mg ²⁺	Br ⁻	0.43267	1.75275	0.0	0.003124	5.0	11
Mg ²⁺	I ⁻	0.49020	1.80413	0.0	0.007934	5.0	11
Mg ²⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		

Table A.2: continued.

cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{\oplus}$	max m	reference
MgOH ⁺	Cl ⁻	-0.10000	1.65800	0.0	0.0		2
MgOH ⁺	SO ₄ ²⁻	0.0	0.0	0.0	0.0		2
MgOH ⁺	HSO ₄ ⁻	0.0	0.0	0.0	0.0		2
MgOH ⁺	CO ₃ ²⁻	0.0	0.0	0.0	0.0		2
MgOH ⁺	HCO ₃ ⁻	0.0	0.0	0.0	0.0		2
MgOH ⁺	OH ⁻	0.0	0.0	0.0	0.0		2
MgOH ⁺	Br ⁻	missing	missing	0.0	missing		
MgOH ⁺	I ⁻	missing	missing	0.0	missing		
MgOH ⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
H ⁺	Cl ⁻	0.17750	0.29450	0.0	0.000800	6.0	2,11
H ⁺	SO ₄ ²⁻	0.02170	0.0	0.0	0.041100	6.0	18
H ⁺	HSO ₄ ⁻	0.21060	0.53200	0.0	0.0	6.0	18
H ⁺	CO ₃ ²⁻	0.0	0.0	0.0	0.0		2,8
H ⁺	HCO ₃ ⁻	0.0	0.0	0.0	0.0		2,8
H ⁺	OH ⁻	0.0	0.0	0.0	0.0		2
H ⁺	Br ⁻	0.19600	0.35640	0.0	0.008270	3.0	11
H ⁺	I ⁻	0.23620	0.39200	0.0	0.001100	3.0	11
H ⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
Mn ²⁺	Cl ⁻	0.33223	1.51463	0.0	-0.022688	4.0	16
Mn ²⁺	SO ₄ ²⁻	0.21300	2.93800	-41.906	0.015510	5.0	16
Mn ²⁺	HSO ₄ ⁻	missing	missing	0.0	missing		
Mn ²⁺	CO ₃ ²⁻	missing	missing	missing	missing		
Mn ²⁺	HCO ₃ ⁻	missing	missing	0.0	missing		
Mn ²⁺	OH ⁻	missing	missing	0.0	missing		
Mn ²⁺	Br ⁻	missing	missing	0.0	missing		
Mn ²⁺	I ⁻	missing	missing	0.0	missing		
Mn ²⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
Fe ²⁺	Cl ⁻	0.33593	1.53225	0.0	-0.008607	2.0	11
Fe ²⁺	SO ₄ ²⁻	0.25680	3.06300	-42.000	0.020900	6.0	18
Fe ²⁺	HSO ₄ ⁻	0.42730	3.48000	0.0	0.0	6.0	18
Fe ²⁺	CO ₃ ²⁻	missing	missing	missing	missing		
Fe ²⁺	HCO ₃ ⁻	missing	missing	0.0	missing		
Fe ²⁺	OH ⁻	missing	missing	0.0	missing		
Fe ²⁺	Br ⁻	missing	missing	0.0	missing		
Fe ²⁺	I ⁻	missing	missing	0.0	missing		
Fe ²⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		

Table A.2: continued.

cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^2	max m	reference
Sr^{2+}	Cl^-	0.28575	1.66725	0.0	-0.001305	4.0	11,17
Sr^{2+}	SO_4^{2-}	0.20000	3.19730	-78.000	0.0	5.0	17
Sr^{2+}	HSO_4^-	missing	missing	0.0	missing		
Sr^{2+}	CO_3^{2-}	missing	missing	missing	missing		
Sr^{2+}	HCO_3^-	missing	missing	0.0	missing		
Sr^{2+}	OH^-	missing	missing	0.0	missing		
Sr^{2+}	Br^-	0.33113	1.71150	0.0	0.001225	2.0	11
Sr^{2+}	I^-	0.40125	1.86000	0.0	0.002657	2.0	11
Sr^{2+}	Al(OH)_4^-	missing	missing	0.0	missing		
Ba^{2+}	Cl^-	0.26280	1.49625	0.0	-0.019378	1.8	11
Ba^{2+}	SO_4^{2-}	missing	missing	missing	missing		
Ba^{2+}	HSO_4^-	missing	missing	0.0	missing		
Ba^{2+}	CO_3^{2-}	missing	missing	missing	missing		
Ba^{2+}	HCO_3^-	missing	missing	0.0	missing		
Ba^{2+}	OH^-	0.17175	1.20000	0.0	0.0	0.1	11
Ba^{2+}	Br^-	0.31455	1.56975	0.0	-0.015958	2.0	11
Ba^{2+}	I^-	0.42188	1.68675	0.0	-0.017427	1.8	11
Ba^{2+}	Al(OH)_4^-	missing	missing	0.0	missing		
Li^+	Cl^-	0.14940	0.30740	0.0	0.003590	6.0	11
Li^+	SO_4^{2-}	0.13628	1.27050	0.0	-0.003993	3.0	11
Li^+	HSO_4^-	missing	missing	0.0	missing		
Li^+	CO_3^{2-}	missing	missing	0.0	missing		
Li^+	HCO_3^-	missing	missing	0.0	missing		
Li^+	OH^-	0.01500	0.14000	0.0	0.0	4.0	11
Li^+	Br^-	0.17480	0.25470	0.0	0.005300	2.5	11
Li^+	I^-	0.21040	0.37300	0.0	0.0	1.4	11
Li^+	Al(OH)_4^-	missing	missing	0.0	missing		
Al^{3+}	Cl^-	0.69933	5.84467	0.0	0.002733	1.6	11
Al^{3+}	SO_4^{2-}	0.85400	18.5300	-500.000	-0.091100	13.0	23
Al^{3+}	HSO_4^-	missing	missing	0.0	missing		
Al^{3+}	CO_3^{2-}	missing	missing	missing	missing		
Al^{3+}	HCO_3^-	missing	missing	0.0	missing		
Al^{3+}	OH^-	0.0	0.0	0.0	0.0		
Al^{3+}	Br^-	missing	missing	0.0	missing		
Al^{3+}	I^-	missing	missing	0.0	missing		
Al^{3+}	Al(OH)_4^-	missing	missing	0.0	missing		

Table A.2: continued.

cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^2	max m	reference
AlOH ²⁺	Cl ⁻	missing	missing	0.0	missing		
AlOH ²⁺	SO ₄ ²⁻	missing	missing	0.0	missing		
AlOH ²⁺	HSO ₄ ⁻	missing	missing	0.0	missing		
AlOH ²⁺	CO ₃ ²⁻	missing	missing	missing	missing		
AlOH ²⁺	HCO ₃ ⁻	missing	missing	0.0	missing		
AlOH ²⁺	OH ⁻	0.0	0.0	0.0	0.0		
AlOH ²⁺	Br ⁻	missing	missing	0.0	missing		
AlOH ²⁺	I ⁻	missing	missing	0.0	missing		
AlOH ²⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	Cl ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	SO ₄ ²⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	HSO ₄ ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	CO ₃ ²⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	HCO ₃ ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	OH ⁻	0.0	0.0	0.0	0.0		
Al(OH) ₂ ⁺	Br ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	I ⁻	missing	missing	0.0	missing		
Al(OH) ₂ ⁺	Al(OH) ₄ ⁻	missing	missing	0.0	missing		

missing values have been approximated as follows:

Na ⁺	Al(OH) ₄ ⁻	=	Na ⁺	OH ⁻	K ⁺	Al(OH) ₄ ⁻	=	K ⁺	OH ⁻
Ca ²⁺	Al(OH) ₄ ⁻	=	Ca ²⁺	OH ⁻	Mg ²⁺	Al(OH) ₄ ⁻	=	Mg ²⁺	OH ⁻
Ba ²⁺	Al(OH) ₄ ⁻	=	Ba ²⁺	OH ⁻	Li ⁺	Al(OH) ₄ ⁻	=	Li ⁺	OH ⁻
Sr ²⁺	Al(OH) ₄ ⁻	=	Ba ²⁺	OH ⁻	Sr ²⁺	OH ⁻	=	Ba ²⁺	OH ⁻
Ba ²⁺	SO ₄ ²⁻	=	Sr ²⁺	SO ₄ ²⁻	Sr ²⁺	CO ₃ ²⁻	=	Ca ²⁺	CO ₃ ²⁻
Ba ²⁺	CO ₃ ²⁻	=	Ca ²⁺	CO ₃ ²⁻	Sr ²⁺	HCO ₃ ⁻	=	Ca ²⁺	HCO ₃ ⁻
Ba ²⁺	HCO ₃ ⁻	=	Ca ²⁺	HCO ₃ ⁻	AlOH ²⁺	Cl ⁻	=	Ca ²⁺	Cl ⁻
AlOH ²⁺	SO ₄ ²⁻	=	Ca ²⁺	SO ₄ ²⁻	AlOH ²⁺	HSO ₄ ⁻	=	Ca ²⁺	HSO ₄ ⁻
AlOH ²⁺	CO ₃ ²⁻	=	Ca ²⁺	CO ₃ ²⁻	AlOH ²⁺	HCO ₃ ⁻	=	Ca ²⁺	HCO ₃ ⁻
Al(OH) ₂ ⁺	Cl ⁻	=	Na ⁺	Cl ⁻)	Al(OH) ₂ ⁺	SO ₄ ²⁻	=	Na ⁺	SO ₄ ²⁻
Al(OH) ₂ ⁺	HSO ₄ ⁻	=	Na ⁺	HSO ₄ ⁻	Al(OH) ₂ ⁺	CO ₃ ²⁻	=	Na ⁺	CO ₃ ²⁻
Al(OH) ₂ ⁺	HCO ₃ ⁻	=	Na ⁺	HCO ₃ ⁻					
MgOH ⁺	Br ⁻	=	0.0	MgOH ⁺	I ⁻	=	0.0	MgOH ⁺	Al(OH) ₄ ⁻ = 0.0
H ⁺	Al(OH) ₄ ⁻	=	0.0	Mn ²⁺	HSO ₄ ⁻	=	0.0	Mn ²⁺	CO ₃ ²⁻ = 0.0
Mn ²⁺	HCO ₃ ⁻	=	0.0	Mn ²⁺	OH ⁻	=	0.0	Mn ²⁺	Br ⁻ = 0.0
Mn ²⁺	I ⁻	=	0.0	Mn ²⁺	Al(OH) ₄ ⁻	=	0.0	Fe ²⁺	CO ₃ ²⁻ = 0.0
Fe ²⁺	HCO ₃ ⁻	=	0.0	Fe ²⁺	OH ⁻	=	0.0	Fe ²⁺	Br ⁻ = 0.0
Fe ²⁺	I ⁻	=	0.0	Fe ²⁺	Al(OH) ₄ ⁻	=	0.0	Al ³⁺	Al(OH) ₄ ⁻ = 0.0
Ba ²⁺	Al(OH) ₄ ⁻	=	0.0	Li ⁺	HSO ₄ ⁻	=	0.0	Li ⁺	CO ₃ ²⁻ = 0.0
Li ⁺	HCO ₃ ⁻	=	0.0	AlOH ²⁺	OH ⁻	=	0.0	AlOH ²⁺	Br ⁻ = 0.0
AlOH ²⁺	I ⁻	=	0.0	AlOH ²⁺	Al(OH) ₄ ⁻	=	0.0	Al(OH) ₂ ⁺	OH ⁻ = 0.0
Al(OH) ₂ ⁺	Br ⁻	=	0.0	Al(OH) ₂ ⁺	I ⁻	=	0.0	Al(OH) ₂ ⁺	Al(OH) ₄ ⁻ = 0.0

Table A.3: Ion interaction parameters: θ_{cc} and θ_{ce} at 25°C.

cation	cation	θ	max I	reference	θ	max I	reference
Na ⁺	K ⁺	-0.0120		2	-0.1540	6.0	3
Na ⁺	Ca ²⁺	0.0700	8.0	2,10	-0.0078	6.0	4
Na ⁺	Mg ²⁺	0.0700	5.9	2,10	0.0	9.0	12
Na ⁺	MgOH ⁺	0.0		2	missing		
Na ⁺	H ⁺	0.0360		2	0.0360	3.0	12
Na ⁺	Mn ²⁺	0.0820	5.5	10	-0.0030	5.5	12
Na ⁺	Fe ²⁺	missing			missing		
Na ⁺	Sr ²⁺	0.0510	5.0	17	0.0094	6.2	15
Na ⁺	Ba ²⁺	0.0670	5.0	10	-0.0030	5.0	12
Na ⁺	Li ⁺	0.0120	6.0	12	0.0120	6.0	12
Na ⁺	Al ³⁺	missing			missing		
Na ⁺	AlOH ²⁺	missing			missing		
Na ⁺	Al(OH) ₂ ⁺	missing			missing		
K ⁺	Ca ²⁺	0.0320	5.0	2,10	-0.0400	5.0	12
K ⁺	Mg ²⁺	0.0		2	missing		
K ⁺	MgOH ⁺	0.0		2	missing		
K ⁺	H ⁺	0.0050		2	0.0050	3.5	12
K ⁺	Mn ²⁺	missing			missing		
K ⁺	Fe ²⁺	missing			missing		
K ⁺	Sr ²⁺	missing			missing		
K ⁺	Ba ²⁺	0.0100	5.0	10	-0.0720	5.0	12
K ⁺	Li ⁺	-0.0220	4.8	12	-0.0220	4.8	12
K ⁺	Al ³⁺	missing			missing		
K ⁺	AlOH ²⁺	missing			missing		
K ⁺	Al(OH) ₂ ⁺	missing			missing		
Ca ²⁺	Mg ²⁺	0.0070		2	0.0100	7.7	12
Ca ²⁺	MgOH ⁺	0.0		2	missing		
Ca ²⁺	H ⁺	0.0920		2	-0.0333	5.0	14
Ca ²⁺	Mn ²⁺	missing			missing		
Ca ²⁺	Fe ²⁺	missing			missing		
Ca ²⁺	Sr ²⁺	missing			missing		
Ca ²⁺	Ba ²⁺	missing			missing		
Ca ²⁺	Li ⁺	missing			missing		
Ca ²⁺	Al ³⁺	0.0	1.0	23	missing		
Ca ²⁺	AlOH ²⁺	missing			missing		

Table A.3: continued.

cation	cation	θ	max I	reference	θ	max I	reference
Ca ²⁺	Al(OH) ₂ ⁺	missing			missing		
Mg ²⁺	MgOH ⁺	0.0		2	missing		
Mg ²⁺	H ⁺	0.1000		2	-0.0240	5.0	20
Mg ²⁺	Mn ²⁺	missing			missing		
Mg ²⁺	Fe ²⁺	missing			missing		
Mg ²⁺	Sr ²⁺	missing			missing		
Mg ²⁺	Ba ²⁺	missing			missing		
Mg ²⁺	Li ⁺	missing			missing		
Mg ²⁺	Al ³⁺	0.0	13.0	23	missing		
Mg ²⁺	AlOH ²⁺	missing			missing		
Mg ²⁺	Al(OH) ₂ ⁺	missing			missing		
MgOH ⁺	H ⁺	0.0		2	missing		
MgOH ⁺	Mn ²⁺	missing			missing		
MgOH ⁺	Fe ²⁺	missing			missing		
MgOH ⁺	Sr ²⁺	missing			missing		
MgOH ⁺	Ba ²⁺	missing			missing		
MgOH ⁺	Li ⁺	missing			missing		
MgOH ⁺	Al ³⁺	missing			missing		
MgOH ⁺	AlOH ²⁺	missing			missing		
MgOH ⁺	Al(OH) ₂ ⁺	missing			missing		
H ⁺	Mn ²⁺	0.0834	5.0	21	-0.0010	5.0	21
H ⁺	Fe ²⁺	3.5000	6.0	18	missing		
H ⁺	Sr ²⁺	0.0	5.0	17	-0.0200	8.0	12
H ⁺	Ba ²⁺	0.0720	3.0	10	-0.0360	3.0	12
H ⁺	Li ⁺	0.0150	2.5	12	0.0150	2.5	12
H ⁺	Al ³⁺	0.1850	?	10	missing		
H ⁺	AlOH ²⁺	missing			missing		
H ⁺	Al(OH) ₂ ⁺	missing			missing		
Mn ²⁺	Fe ²⁺	missing			missing		
Mn ²⁺	Sr ²⁺	missing			missing		
Mn ²⁺	Ba ²⁺	missing			missing		
Mn ²⁺	Li ⁺	missing			missing		
Mn ²⁺	Al ³⁺	missing			missing		
Mn ²⁺	AlOH ²⁺	missing			missing		
Mn ²⁺	Al(OH) ₂ ⁺	missing			missing		

Table A.3: continued.

cation	cation	θ	max I	reference	θ	max I	reference
Fe ²⁺	Sr ²⁺	missing			missing		
Fe ²⁺	Ba ²⁺	missing			missing		
Fe ²⁺	Li ⁺	missing			missing		
Fe ²⁺	Al ³⁺	0.0	12.0	23	missing		
Fe ²⁺	AlOH ²⁺	missing			missing		
Fe ²⁺	Al(OH) ₂ ⁺	missing			missing		
Sr ²⁺	Ba ²⁺	missing			missing		
Sr ²⁺	Li ⁺	missing			missing		
Sr ²⁺	Al ³⁺	missing			missing		
Sr ²⁺	AlOH ²⁺	missing			missing		
Sr ²⁺	Al(OH) ₂ ⁺	missing			missing		
Ba ²⁺	Li ⁺	0.0	4.3	10	-0.0700	4.3	12
Ba ²⁺	Al ³⁺	missing			missing		
Ba ²⁺	AlOH ²⁺	missing			missing		
Ba ²⁺	Al(OH) ₂ ⁺	missing			missing		
Li ⁺	Al ³⁺	missing			missing		
Li ⁺	AlOH ²⁺	missing			missing		
Li ⁺	Al(OH) ₂ ⁺	missing			missing		
Al ³⁺	AlOH ²⁺	missing			missing		
Al ³⁺	Al(OH) ₂ ⁺	missing			missing		
AlOH ²⁺	Al(OH) ₂ ⁺	missing			missing		

Table A.4: Ion interaction parameters: ${}^{\circ}\theta_{aa}$ and θ_{aa} at 25°C.

anion	anion	${}^{\circ}\theta$	max I	reference	θ	max I	reference
Cl ⁻	SO ₄ ²⁻	0.0200		2,17	-0.0200	9.0	1
Cl ⁻	HSO ₄ ⁻	-0.0060		2	-0.0060		2
Cl ⁻	CO ₃ ²⁻	-0.0200	1.0	2,8	-0.0920	3.0	9
Cl ⁻	HCO ₃ ⁻	0.0359	1.0	8,9	0.0359	3.0	8,9
Cl ⁻	OH ⁻	-0.0500	1.0	2,8,10	-0.0500	3.5	12
Cl ⁻	Br ⁻	0.0	4.4	12	0.0	4.4	12
Cl ⁻	I ⁻	missing			missing		
Cl ⁻	Al(OH) ₄ ⁻	missing			missing		
SO ₄ ²⁻	HSO ₄ ⁻	0.0		2,18	0.0	6.0	13
SO ₄ ²⁻	CO ₃ ²⁻	0.0200		2	0.0200		2
SO ₄ ²⁻	HCO ₃ ⁻	0.0100		2	missing		
SO ₄ ²⁻	OH ⁻	-0.0130		2	missing		
SO ₄ ²⁻	Br ⁻	missing			missing		
SO ₄ ²⁻	I ⁻	missing			missing		
SO ₄ ²⁻	Al(OH) ₄ ⁻	missing			missing		
HSO ₄ ⁻	CO ₃ ²⁻	0.0		2	missing		
HSO ₄ ⁻	HCO ₃ ⁻	0.0		2	0.0		2
HSO ₄ ⁻	OH ⁻	0.0		2	0.0		2
HSO ₄ ⁻	Br ⁻	missing			missing		
HSO ₄ ⁻	I ⁻	missing			missing		
HSO ₄ ⁻	Al(OH) ₄ ⁻	missing			missing		
CO ₃ ²⁻	HCO ₃ ⁻	-0.0400		2,8	-0.0630	7.0	22
CO ₃ ²⁻	OH ⁻	0.0	1.0	8,9	0.0	1.0	8,9
CO ₃ ²⁻	Br ⁻	missing			missing		
CO ₃ ²⁻	I ⁻	missing			missing		
CO ₃ ²⁻	Al(OH) ₄ ⁻	missing			missing		
HCO ₃ ⁻	OH ⁻	0.0		2,8	0.0	1.0	2,8
HCO ₃ ⁻	Br ⁻	missing			missing		
HCO ₃ ⁻	I ⁻	missing			missing		
HCO ₃ ⁻	Al(OH) ₄ ⁻	missing			missing		
OH ⁻	Br ⁻	-0.0650	3.0	12	-0.0650	3.0	12
OH ⁻	I ⁻	missing			missing		
OH ⁻	Al(OH) ₄ ⁻	missing			missing		
Br ⁻	I ⁻	missing			missing		
Br ⁻	Al(OH) ₄ ⁻	missing			missing		
I ⁻	Al(OH) ₄ ⁻	missing			missing		

Table A.5: Ion interaction parameters: ${}^a\psi_{cca}$ and ψ_{cca} at 25°C.

cation	cation	anion	${}^a\psi$	max I	reference	ψ	max I	reference
Na ⁺	K ⁺	Cl ⁻	-0.0018		2	-0.0154	6.0	3
Na ⁺	K ⁺	SO ₄ ²⁻	-0.0100		11	-0.0100	3.6	12
Na ⁺	K ⁺	HSO ₄ ⁻	0.0		2	missing		
Na ⁺	K ⁺	CO ₃ ²⁻	0.0030		2	missing		
Na ⁺	K ⁺	HCO ₃ ⁻	-0.0030		2	missing		
Na ⁺	K ⁺	OH ⁻	0.0		2	missing		
Na ⁺	K ⁺	Br ⁻	missing			-0.0022	4.8	12
Na ⁺	Ca ²⁺	Cl ⁻	-0.0070	8.0	2,10	0.0029	6.0	4
Na ⁺	Ca ²⁺	SO ₄ ²⁻	-0.0550		2	missing		
Na ⁺	Ca ²⁺	HSO ₄ ⁻	0.0		2	missing		
Na ⁺	Ca ²⁺	CO ₃ ²⁻	0.0		2	missing		
Na ⁺	Ca ²⁺	HCO ₃ ⁻	0.0		2	missing		
Na ⁺	Ca ²⁺	OH ⁻	0.0		2	missing		
Na ⁺	Mg ²⁺	Cl ⁻	-0.0120		2	0.0	5.9	12
Na ⁺	Mg ²⁺	SO ₄ ²⁻	-0.0150		2	0.0	9.0	12
Na ⁺	Mg ²⁺	HSO ₄ ⁻	0.0		2	missing		
Na ⁺	Mg ²⁺	CO ₃ ²⁻	0.0		2	missing		
Na ⁺	Mg ²⁺	HCO ₃ ⁻	0.0		2	missing		
Na ⁺	Mg ²⁺	OH ⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	Cl ⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	SO ₄ ²⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	HSO ₄ ⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	CO ₃ ²⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	HCO ₃ ⁻	0.0		2	missing		
Na ⁺	MgOH ⁺	OH ⁻	0.0		2	missing		
Na ⁺	H ⁺	Cl ⁻	-0.0040		2	-0.0040	3.0	12
Na ⁺	H ⁺	SO ₄ ²⁻	0.0		2	missing		
Na ⁺	H ⁺	HSO ₄ ⁻	-0.0129		2	missing		
Na ⁺	H ⁺	CO ₃ ²⁻	0.0		2	missing		
Na ⁺	H ⁺	HCO ₃ ⁻	0.0		2	missing		
Na ⁺	H ⁺	OH ⁻	0.0		2	missing		
Na ⁺	H ⁺	Br ⁻	missing			-0.0120	3.0	12
Na ⁺	Mn ²⁺	Cl ⁻	-0.0174	5.5	10	0.0	5.5	12
Na ⁺	Sr ²⁺	Cl ⁻	-0.0210	5.0	17	-0.0032	6.2	15
Na ⁺	Sr ²⁺	SO ₄ ²⁻	0.0	5.0	17	missing		

Table A.5: continued.

cation	cation	anion	ψ	max I	reference	ψ	max I	reference
Na ⁺	Ba ²⁺	Cl ⁻	-0.0120	5.0	10	0.0	5.0	12
Na ⁺	Li ⁺	Cl ⁻	-0.0030	6.0	12	-0.0030	6.0	12
K ⁺	Ca ²⁺	Cl ⁻	-0.0250	5.0	2,10	-0.0150	5.0	12
K ⁺	Ca ²⁺	SO ₄ ²⁻	0.0		2	missing		
K ⁺	Ca ²⁺	HSO ₄ ⁻	0.0		2	missing		
K ⁺	Ca ²⁺	CO ₃ ²⁻	0.0		2	missing		
K ⁺	Ca ²⁺	HCO ₃ ⁻	0.0		2	missing		
K ⁺	Ca ²⁺	OH ⁻	0.0		2	missing		
K ⁺	Mg ²⁺	Cl ⁻	-0.0220		2	missing		
K ⁺	Mg ²⁺	SO ₄ ²⁻	-0.0480		2	missing		
K ⁺	Mg ²⁺	HSO ₄ ⁻	0.0		2	missing		
K ⁺	Mg ²⁺	CO ₃ ²⁻	0.0		2	missing		
K ⁺	Mg ²⁺	HCO ₃ ⁻	0.0		2	missing		
K ⁺	Mg ²⁺	OH ⁻	0.0		2	missing		
K ⁺	MgOH ⁺	Cl ⁻	0.0		2	missing		
K ⁺	MgOH ⁺	SO ₄ ²⁻	0.0		2	missing		
K ⁺	MgOH ⁺	HSO ₄ ⁻	0.0		2	missing		
K ⁺	MgOH ⁺	CO ₃ ²⁻	0.0		2	missing		
K ⁺	MgOH ⁺	HCO ₃ ⁻	0.0		2	missing		
K ⁺	MgOH ⁺	OH ⁻	0.0		2	missing		
K ⁺	H ⁺	Cl ⁻	-0.0110		2	-0.0110	3.5	2
K ⁺	H ⁺	SO ₄ ²⁻	0.1970		2	missing		
K ⁺	H ⁺	HSO ₄ ⁻	-0.0265		2	missing		
K ⁺	H ⁺	CO ₃ ²⁻	0.0		2	missing		
K ⁺	H ⁺	HCO ₃ ⁻	0.0		2	missing		
K ⁺	H ⁺	OH ⁻	0.0		2	missing		
K ⁺	H ⁺	Br ⁻	missing			-0.0210	3.0	12
K ⁺	Ba ²⁺	Cl ⁻	-0.0170	5.0	10	0.0	5.0	12
K ⁺	Li ⁺	Cl ⁻	-0.0100	4.8	12	-0.0100	4.8	12
Ca ²⁺	Mg ²⁺	Cl ⁻	-0.0120		2	0.0	7.7	12
Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	0.0240		2	missing		
Ca ²⁺	Mg ²⁺	HSO ₄ ⁻	0.0		2	missing		
Ca ²⁺	Mg ²⁺	CO ₃ ²⁻	0.0		2	missing		
Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	0.0		2	missing		
Ca ²⁺	Mg ²⁺	OH ⁻	0.0		2	missing		

Table A.5: continued.

cation	cation	anion	ψ	max I	reference	ψ	max I	reference
Ca ²⁺	MgOH ⁺	Cl ⁻	0.0		2	missing		
Ca ²⁺	MgOH ⁺	SO ₄ ²⁻	0.0		2	missing		
Ca ²⁺	MgOH ⁺	HSO ₄ ⁻	0.0		2	missing		
Ca ²⁺	MgOH ⁺	CO ₃ ²⁻	0.0		2	missing		
Ca ²⁺	MgOH ⁺	HCO ₃ ⁻	0.0		2	missing		
Ca ²⁺	MgOH ⁺	OH ⁻	0.0		2	missing		
Ca ²⁺	H ⁺	Cl ⁻	-0.0150		2	0.0160	5.0	14
Ca ²⁺	H ⁺	SO ₄ ²⁻	0.0		2	missing		
Ca ²⁺	H ⁺	HSO ₄ ⁻	0.0		2	missing		
Ca ²⁺	H ⁺	CO ₃ ²⁻	0.0		2	missing		
Ca ²⁺	H ⁺	HCO ₃ ⁻	0.0		2	missing		
Ca ²⁺	H ⁺	OH ⁻	0.0		2	missing		
Ca ²⁺	H ⁺	Br ⁻	0.0163	2.0	5	0.0918	2.0	5
Ca ²⁺	Al ³⁺	SO ₄ ²⁻	0.0300	1.0	23	missing		
Mg ²⁺	MgOH ⁺	Cl ⁻	0.0280		2	missing		
Mg ²⁺	MgOH ⁺	SO ₄ ²⁻	0.0		2	missing		
Mg ²⁺	MgOH ⁺	HSO ₄ ⁻	0.0		2	missing		
Mg ²⁺	MgOH ⁺	CO ₃ ²⁻	0.0		2	missing		
Mg ²⁺	MgOH ⁺	HCO ₃ ⁻	0.0		2	missing		
Mg ²⁺	MgOH ⁺	OH ⁻	0.0		2	missing		
Mg ²⁺	H ⁺	Cl ⁻	-0.0110		2	0.0124	5.0	20
Mg ²⁺	H ⁺	SO ₄ ²⁻	0.0		2	missing		
Mg ²⁺	H ⁺	HSO ₄ ⁻	-0.0178		2	missing		
Mg ²⁺	H ⁺	CO ₃ ²⁻	0.0		2	missing		
Mg ²⁺	H ⁺	HCO ₃ ⁻	0.0		2	missing		
Mg ²⁺	H ⁺	OH ⁻	0.0		2	missing		
Mg ²⁺	H ⁺	Br ⁻	-0.0050	4.0	14	0.0180	4.0	14
Mg ²⁺	Al ³⁺	SO ₄ ²⁻	0.0300	13.0	23	missing		
MgOH ⁺	H ⁺	Cl ⁻	0.0		2	missing		
MgOH ⁺	H ⁺	SO ₄ ²⁻	0.0		2	missing		
MgOH ⁺	H ⁺	HSO ₄ ⁻	0.0		2	missing		
MgOH ⁺	H ⁺	CO ₃ ²⁻	0.0		2	missing		
MgOH ⁺	H ⁺	HCO ₃ ⁻	0.0		2	missing		
MgOH ⁺	H ⁺	OH ⁻	0.0		2	missing		
H ⁺	Mn ²⁺	Cl ⁻	-0.0090	5.0	21	0.0014	5.0	21

Table A.5: continued.

cation	cation	anion	ψ	max I	reference	ψ	max I	reference
H ⁺	Fe ²⁺	SO ₄ ²⁻	0.0	6.0	18	missing		
H ⁺	Fe ²⁺	HSO ₄ ⁻	0.0143	6.0	18	missing		
H ⁺	Sr ²⁺	Cl ⁻	0.0	5.0	17	0.0180	8.0	12
H ⁺	Ba ²⁺	Cl ⁻	0.0	3.0	10	0.0240	3.0	12
H ⁺	Ba ²⁺	Br ⁻	0.0057	2.0	6	0.0812	2.0	6
H ⁺	Li ⁺	Cl ⁻	0.0	5.0	12	0.0	5.0	12
H ⁺	Li ⁺	Br ⁻	missing			0.0	2.5	12
H ⁺	Al ³⁺	Cl ⁻	0.0130	?	10	missing		
Ba ²⁺	Li ⁺	Cl ⁻	0.0090	4.3	10	0.0190	4.3	12
Fe ²⁺	Al ³⁺	SO ₄ ²⁻	0.0	12.0	23	missing		

Table A.6: Ion interaction parameters: ${}^{\circ}\psi_{\text{aac}}$ and ψ_{aac} at 25°C.

anion	anion	cation	${}^{\circ}\psi$	max I	reference	ψ	max I	reference
Cl ⁻	SO ₄ ²⁻	Na ⁺	0.0014		2,17	0.0040	9.0	1
Cl ⁻	SO ₄ ²⁻	K ⁺	0.0		2	-0.0070	2.3	1
Cl ⁻	SO ₄ ²⁻	Ca ²⁺	-0.0180		2	missing		
Cl ⁻	SO ₄ ²⁻	Mg ²⁺	-0.0040		2	-0.0070	7.0	1
Cl ⁻	SO ₄ ²⁻	MgOH ⁺	0.0		2	missing		
Cl ⁻	SO ₄ ²⁻	H ⁺	0.0		2	missing		
Cl ⁻	SO ₄ ²⁻	Sr ²⁺	0.0	5.0	17	missing		
Cl ⁻	HSO ₄ ⁻	Na ⁺	-0.0060		2	missing		
Cl ⁻	HSO ₄ ⁻	K ⁺	0.0		2	missing		
Cl ⁻	HSO ₄ ⁻	Ca ²⁺	0.0		2	missing		
Cl ⁻	HSO ₄ ⁻	Mg ²⁺	0.0		2	missing		
Cl ⁻	HSO ₄ ⁻	MgOH ⁺	0.0		2	missing		
Cl ⁻	HSO ₄ ⁻	H ⁺	0.0130		2	missing		
Cl ⁻	CO ₃ ²⁻	Na ⁺	0.0085		2,8	0.0	3.0	9
Cl ⁻	CO ₃ ²⁻	K ⁺	0.0040		2	0.0073	7.0	22
Cl ⁻	CO ₃ ²⁻	Ca ²⁺	0.0		2	missing		
Cl ⁻	CO ₃ ²⁻	Mg ²⁺	0.0		2	missing		
Cl ⁻	CO ₃ ²⁻	MgOH ⁺	0.0		2	missing		
Cl ⁻	CO ₃ ²⁻	H ⁺	0.0		2	missing		
Cl ⁻	HCO ₃ ⁻	Na ⁺	-0.0143	3.0	8,9	-0.0143	3.0	9
Cl ⁻	HCO ₃ ⁻	K ⁺	0.0		2	-0.0037	7.0	22
Cl ⁻	HCO ₃ ⁻	Ca ²⁺	0.0		2	missing		
Cl ⁻	HCO ₃ ⁻	Mg ²⁺	-0.0960		2	missing		
Cl ⁻	HCO ₃ ⁻	MgOH ⁺	0.0		2	missing		
Cl ⁻	HCO ₃ ⁻	H ⁺	0.0		2	missing		
Cl ⁻	OH ⁻	Na ⁺	-0.0060		2,8,11	-0.0060	3.0	12
Cl ⁻	OH ⁻	K ⁺	-0.0060		2	-0.0080	3.5	12
Cl ⁻	OH ⁻	Ca ²⁺	-0.0250		2	missing		
Cl ⁻	OH ⁻	Mg ²⁺	0.0		2	missing		
Cl ⁻	OH ⁻	MgOH ⁺	0.0		2	missing		
Cl ⁻	OH ⁻	H ⁺	0.0		2	missing		
Cl ⁻	Br ⁻	Na ⁺	missing			0.0	4.4	12
Cl ⁻	Br ⁻	K ⁺	missing			0.0	4.4	12
SO ₄ ²⁻	HSO ₄ ⁻	Na ⁺	-0.0094		2	missing		
SO ₄ ²⁻	HSO ₄ ⁻	K ⁺	-0.0677		2	missing		

Table A.6: continued.

anion	anion	cation	ψ	max I	reference	ψ	max I	reference
SO ₄ ²⁻	HSO ₄ ⁻	Ca ²⁺	0.0		2	missing		
SO ₄ ²⁻	HSO ₄ ⁻	Mg ²⁺	-0.0425		2	missing		
SO ₄ ²⁻	HSO ₄ ⁻	MgOH ⁺	0.0		2	missing		
SO ₄ ²⁻	HSO ₄ ⁻	H ⁺	0.0	6.0	2,18	0.0	6.0	13
SO ₄ ²⁻	HSO ₄ ⁻	Fe ²⁺	0.0	6.0	18	missing		
SO ₄ ²⁻	CO ₃ ²⁻	Na ⁺	-0.0050		2	missing		
SO ₄ ²⁻	CO ₃ ²⁻	K ⁺	-0.0090		2	missing		
SO ₄ ²⁻	CO ₃ ²⁻	Ca ²⁺	0.0		2	missing		
SO ₄ ²⁻	CO ₃ ²⁻	Mg ²⁺	0.0		2	missing		
SO ₄ ²⁻	CO ₃ ²⁻	MgOH ⁺	0.0		2	missing		
SO ₄ ²⁻	CO ₃ ²⁻	H ⁺	0.0		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	-0.0050		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	K ⁺	0.0		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	Ca ²⁺	0.0		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	Mg ²⁺	-0.1610		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	MgOH ⁺	0.0		2	missing		
SO ₄ ²⁻	HCO ₃ ⁻	H ⁺	0.0		2	missing		
SO ₄ ²⁻	OH ⁻	Na ⁺	-0.0090		2	missing		
SO ₄ ²⁻	OH ⁻	K ⁺	-0.0500		2	missing		
SO ₄ ²⁻	OH ⁻	Ca ²⁺	0.0		2	missing		
SO ₄ ²⁻	OH ⁻	Mg ²⁺	0.0		2	missing		
SO ₄ ²⁻	OH ⁻	MgOH ⁺	0.0		2	missing		
SO ₄ ²⁻	OH ⁻	H ⁺	0.0		2	missing		
HSO ₄ ⁻	CO ₃ ²⁻	Na ⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	K ⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Ca ²⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Mg ²⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	MgOH ⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	H ⁺	0.0		2	0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Mn ²⁺	0.0			0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Fe ²⁺	0.0			0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Sr ²⁺	0.0			0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Ba ²⁺	0.0			0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Li ⁺	0.0			0.0		
HSO ₄ ⁻	CO ₃ ²⁻	Al ³⁺	0.0			0.0		

Table A.6: continued.

anion	anion	cation	ψ	max I	reference	ψ	max I	reference
HSO ₄	HCO ₃	Na ⁺	0.0		2	0.0		
HSO ₄	HCO ₃	K ⁺	0.0		2	0.0		
HSO ₄	HCO ₃	Ca ²⁺	0.0		2	0.0		
HSO ₄	HCO ₃	Mg ²⁺	0.0		2	0.0		
HSO ₄	HCO ₃	MgOH ⁺	0.0		2	0.0		
HSO ₄	HCO ₃	H ⁺	0.0		2	0.0		
HSO ₄	HCO ₃	Mn ²⁺	0.0			0.0		
HSO ₄	HCO ₃	Fe ²⁺	0.0			0.0		
HSO ₄	HCO ₃	Sr ²⁺	0.0			0.0		
HSO ₄	HCO ₃	Ba ²⁺	0.0			0.0		
HSO ₄	HCO ₃	Li ⁺	0.0			0.0		
HSO ₄	HCO ₃	Al ³⁺	0.0			0.0		
HSO ₄	OH ⁻	Na ⁺	0.0		2	0.0		
HSO ₄	OH ⁻	K ⁺	0.0		2	0.0		
HSO ₄	OH ⁻	Ca ²⁺	0.0		2	0.0		
HSO ₄	OH ⁻	Mg ²⁺	0.0		2	0.0		
HSO ₄	OH ⁻	MgOH ⁺	0.0		2	0.0		
HSO ₄	OH ⁻	H ⁺	0.0		2	0.0		
HSO ₄	OH ⁻	Mn ²⁺	0.0			0.0		
HSO ₄	OH ⁻	Fe ²⁺	0.0			0.0		
HSO ₄	OH ⁻	Sr ²⁺	0.0			0.0		
HSO ₄	OH ⁻	Ba ²⁺	0.0			0.0		
HSO ₄	OH ⁻	Li ⁺	0.0			0.0		
HSO ₄	OH ⁻	Al ³⁺	0.0			0.0		
CO ₃ ²⁻	HCO ₃	Na ⁺	0.0020		2,8	missing		
CO ₃ ²⁻	HCO ₃	K ⁺	0.0120		2	0.0130	7.02	22
CO ₃ ²⁻	HCO ₃	Ca ²⁺	0.0		2	missing		
CO ₃ ²⁻	HCO ₃	Mg ²⁺	0.0		2	missing		
CO ₃ ²⁻	HCO ₃	MgOH ⁺	0.0		2	missing		
CO ₃ ²⁻	HCO ₃	H ⁺	0.0		2	missing		
CO ₃ ²⁻	OH ⁻	Na ⁺	0.0	1.0	8	missing		
CO ₃ ²⁻	OH ⁻	K ⁺	-0.0100		2	missing		
CO ₃ ²⁻	OH ⁻	Ca ²⁺	0.0		2	missing		
CO ₃ ²⁻	OH ⁻	Mg ²⁺	0.0		2	missing		
CO ₃ ²⁻	OH ⁻	MgOH ⁺	0.0		2	missing		

Table A.6: continued.

anion	anion	cation	ψ	max I	reference	ψ	max I	reference
CO_3^{2-}	OH^-	H^+	0.0		2	missing		
HCO_3^-	OH^-	Na^+	0.0		2,8	missing		
HCO_3^-	OH^-	K^+	0.0		2	missing		
HCO_3^-	OH^-	Ca^{2+}	0.0		2	missing		
HCO_3^-	OH^-	Mg^{2+}	0.0		2	missing		
HCO_3^-	OH^-	MgOH^+	0.0		2	missing		
HCO_3^-	OH^-	H^+	0.0		2	missing		
OH^-	Br^-	Na^+	missing			-0.0180	3.0	12
OH^-	Br^-	K^+	missing			-0.0140	3.0	12

Table A.7: Ion interaction parameters: λ_{nc} and λ_{na} at 25°C.

neutral	cation	λ_{nc}	reference ¹	neutral	anion	λ_{na}	reference ¹
CO ₂ ⁰	Na ⁺	0.100	2	CO ₂ ⁰	Cl ⁻	-0.005	2
CO ₂ ⁰	K ⁺	0.051	2	CO ₂ ⁰	SO ₄ ²⁻	0.097	2
CO ₂ ⁰	Ca ²⁺	0.183	2	CO ₂ ⁰	HSO ₄ ⁻	-0.003	2
CO ₂ ⁰	Mg ²⁺	0.183	2	CO ₂ ⁰	CO ₃ ²⁻	0.0	2
CO ₂ ⁰	MgOH ⁺	0.0	2	CO ₂ ⁰	HCO ₃ ⁻	0.0	2
CO ₂ ⁰	H ⁺	0.0	2	CO ₂ ⁰	OH ⁻	0.0	2
CO ₂ ⁰	Mn ²⁺	0.0		CO ₂ ⁰	Br ⁻	0.0	
CO ₂ ⁰	Fe ²⁺	0.0		CO ₂ ⁰	I ⁻	0.0	
CO ₂ ⁰	Sr ²⁺	0.183		CO ₂ ⁰	Al(OH) ₄ ⁻	0.0	
CO ₂ ⁰	Ba ²⁺	0.0					
CO ₂ ⁰	Li ⁺	0.0					
CO ₂ ⁰	Al ³⁺	0.0					
CO ₂ ⁰	AlOH ²⁺	0.0					
CO ₂ ⁰	Al(OH) ₂ ⁺	0.0					
CaCO ₃ ⁰	Na ⁺	0.0	2	CaCO ₃ ⁰	Cl ⁻	0.0	2
CaCO ₃ ⁰	K ⁺	0.0	2	CaCO ₃ ⁰	SO ₄ ²⁻	0.0	2
CaCO ₃ ⁰	Ca ²⁺	0.0	2	CaCO ₃ ⁰	HSO ₄ ⁻	0.0	2
CaCO ₃ ⁰	Mg ²⁺	0.0	2	CaCO ₃ ⁰	CO ₃ ²⁻	0.0	2
CaCO ₃ ⁰	MgOH ⁺	0.0	2	CaCO ₃ ⁰	HCO ₃ ⁻	0.0	2
CaCO ₃ ⁰	H ⁺	0.0	2	CaCO ₃ ⁰	OH ⁻	0.0	2
CaCO ₃ ⁰	Mn ²⁺	0.0		CaCO ₃ ⁰	Br ⁻	0.0	
CaCO ₃ ⁰	Fe ²⁺	0.0		CaCO ₃ ⁰	I ⁻	0.0	
CaCO ₃ ⁰	Sr ²⁺	0.0		CaCO ₃ ⁰	Al(OH) ₄ ⁻	0.0	
CaCO ₃ ⁰	Ba ²⁺	0.0					
CaCO ₃ ⁰	Li ⁺	0.0					
CaCO ₃ ⁰	Al ³⁺	0.0					
CaCO ₃ ⁰	AlOH ²⁺	0.0					
CaCO ₃ ⁰	Al(OH) ₂ ⁺	0.0					

Table A.7: continued.

neutral	cation	λ_{ac}	reference ¹	neutral	anion	λ_{aa}	reference ¹
MgCO ₃ ⁰	Na ⁺	0.0	2	MgCO ₃ ⁰	Cl ⁻	0.0	2
MgCO ₃ ⁰	K ⁺	0.0	2	MgCO ₃ ⁰	SO ₄ ²⁻	0.0	2
MgCO ₃ ⁰	Ca ²⁺	0.0	2	MgCO ₃ ⁰	HSO ₄ ⁻	0.0	2
MgCO ₃ ⁰	Mg ²⁺	0.0	2	MgCO ₃ ⁰	CO ₃ ²⁻	0.0	2
MgCO ₃ ⁰	MgOH ⁺	0.0	2	MgCO ₃ ⁰	HCO ₃ ⁻	0.0	2
MgCO ₃ ⁰	H ⁺	0.0	2	MgCO ₃ ⁰	OH ⁻	0.0	2
MgCO ₃ ⁰	Mn ²⁺	0.0		MgCO ₃ ⁰	Br ⁻	0.0	
MgCO ₃ ⁰	Fe ²⁺	0.0		MgCO ₃ ⁰	I ⁻	0.0	
MgCO ₃ ⁰	Sr ²⁺	0.0		MgCO ₃ ⁰	Al(OH) ₄ ⁻	0.0	
MgCO ₃ ⁰	Ba ²⁺	0.0					
MgCO ₃ ⁰	Li ⁺	0.0					
MgCO ₃ ⁰	Al ³⁺	0.0					
MgCO ₃ ⁰	AlOH ²⁺	0.0					
MgCO ₃ ⁰	Al(OH) ₂ ⁺	0.0					

1: unreferenced values are estimates

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Table A.8: Coefficients for the interpolation function used to calculate $\beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$, $\beta_{\text{ca}}^{(2)}$ and C_{ca}^{∞} over the temperature range 0°C to 200°C.

Y(T)		a	b	c	d
LiCl	$\beta^{(0)}$	-0.15463×10^{-3}	0.79515×10^{-11}	0.0	0.0
	$\beta^{(1)}$	0.63604×10^{-3}	-0.20272×10^{-9}	0.0	0.0
	C^{∞}	-0.54202×10^{-4}	0.13922×10^{-6}	-0.19939×10^{-9}	-0.58357×10^{-5}
NaCl	$\beta^{(0)}$	0.90108×10^{-3}	-0.57289×10^{-5}	0.10557×10^{-7}	0.53818×10^{-3}
	$\beta^{(1)}$	0.64702×10^{-3}	0.10713×10^{-5}	0.0	0.0
	C^{∞}	-0.13002×10^{-3}	0.63943×10^{-6}	-0.10437×10^{-8}	-0.35192×10^{-4}
KCl	$\beta^{(0)}$	0.70143×10^{-3}	-0.42327×10^{-5}	0.82284×10^{-8}	0.48318×10^{-3}
	$\beta^{(1)}$	0.12099×10^{-2}	-0.12262×10^{-5}	0.36271×10^{-8}	0.26620×10^{-2}
	C^{∞}	-0.74399×10^{-4}	0.44194×10^{-6}	-0.86816×10^{-9}	-0.55653×10^{-4}
CsCl	$\beta^{(0)}$	0.82182×10^{-3}	-0.52680×10^{-5}	0.11424×10^{-7}	0.76925×10^{-3}
	$\beta^{(1)}$	0.18041×10^{-2}	-0.14087×10^{-5}	0.20278×10^{-8}	-0.35167×10^{-3}
	C^{∞}	-0.69008×10^{-4}	0.44147×10^{-6}	-0.92257×10^{-9}	-0.91678×10^{-4}
HCl	$\beta^{(0)}$	0.19074×10^{-1}	-0.24649×10^{-3}	0.88845×10^{-6}	-0.42955×10^{-1}
	$\beta^{(1)}$	0.21784×10^{-3}	0.88333×10^{-5}	-0.70143×10^{-8}	0.27283×10^{-3}
	C^{∞}	---	---	---	---
MgCl ₂	$\beta^{(0)}$	0.32321×10^{-3}	-0.68498×10^{-5}	0.35418×10^{-7}	-0.16178×10^{-3}
	$\beta^{(1)}$	-0.76391×10^{-3}	0.58968×10^{-4}	-0.16970×10^{-6}	0.45708×10^{-2}
	C^{∞}	-0.86988×10^{-4}	0.24120×10^{-6}	-0.34070×10^{-9}	0.16519×10^{-4}
CaCl ₂	$\beta^{(0)}$	-0.67362×10^{-3}	0.47264×10^{-5}	-0.20320×10^{-7}	0.19049×10^{-2}
	$\beta^{(1)}$	0.29703×10^{-2}	0.13518×10^{-4}	-0.63690×10^{-8}	-0.18251×10^{-2}
	C^{∞}	-0.53341×10^{-4}	0.14544×10^{-6}	-0.20188×10^{-9}	-0.11969×10^{-4}
SrCl ₂	$\beta^{(0)}$	0.69640×10^{-3}	-0.83431×10^{-5}	0.24810×10^{-7}	0.75072×10^{-3}
	$\beta^{(1)}$	0.31752×10^{-2}	0.49051×10^{-5}	0.52761×10^{-7}	-0.97344×10^{-3}
	C^{∞}	-0.57620×10^{-4}	0.15896×10^{-6}	-0.22336×10^{-9}	0.37020×10^{-5}
BaCl ₂	$\beta^{(0)}$	0.89444×10^{-3}	-0.75336×10^{-5}	0.13655×10^{-7}	-0.13516×10^{-3}
	$\beta^{(1)}$	0.71761×10^{-2}	-0.34170×10^{-4}	0.18132×10^{-6}	-0.11183×10^{-1}
	C^{∞}	-0.25440×10^{-3}	0.16908×10^{-5}	-0.31178×10^{-1}	-0.51529×10^{-3}
Li ₂ SO ₄	$\beta^{(0)}$	0.63915×10^{-3}	-0.41291×10^{-5}	0.44347×10^{-8}	0.12790×10^{-3}
	$\beta^{(1)}$	0.58838×10^{-2}	-0.85246×10^{-4}	0.44014×10^{-6}	-0.13068×10^{-2}
	C^{∞}	-0.34280×10^{-3}	0.15000×10^{-5}	-0.12871×10^{-8}	0.83980×10^{-3}

Table A.8: continued.

Y(T)	Y(T _R)	a	b	c	d
Na ₂ SO ₄	B ⁽⁰⁾	0.25725x10 ⁻²	-0.15171x10 ⁻⁴	0.32307x10 ⁻⁷	0.31322x10 ⁻²
	B ⁽¹⁾	0.84964x10 ⁻²	-0.66674x10 ⁻⁴	0.26858x10 ⁻⁶	0.45448x10 ⁻²
	C ⁺	-0.39745x10 ⁻³	0.17116x10 ⁻⁵	-0.24303x10 ⁻⁸	-0.11450x10 ⁻²
K ₂ SO ₄	B ⁽⁰⁾	0.14510x10 ⁻²	-0.69712x10 ⁻⁵	0.24159x10 ⁻⁷	0.11649x10 ⁻²
	B ⁽¹⁾		0.80167x10 ⁻²	-0.39371x10 ⁻⁴	0.10856x10 ⁻⁶
	C ⁺	0.10324x10 ⁻³	-0.22638x10 ⁻⁵	0.32108x10 ⁻⁸	-0.23041x10 ⁻³
Cs ₂ SO ₄	B ⁽⁰⁾	0.30808x10 ⁻²	-0.10147x10 ⁻⁴	0.15523x10 ⁻⁷	-0.23765x10 ⁻²
	B ⁽¹⁾	-0.57148x10 ⁻³	-0.52831x10 ⁻⁵	0.24779x10 ⁻⁶	0.35880x10 ⁻¹
	C ⁺	-0.56187x10 ⁻⁴	0.15392x10 ⁻⁶	-0.21473x10 ⁻⁹	-0.62782x10 ⁻⁵
MgSO ₄	B ⁽⁰⁾	0.12004x10 ⁻²	-0.10826x10 ⁻⁴	0.48239x10 ⁻⁷	-0.17922x10 ⁻²
	B ⁽¹⁾	0.12505x10 ⁻¹	-0.49188x10 ⁻⁴	0.29291x10 ⁻⁶	-0.18739x10 ⁻¹
	B ⁽²⁾	-0.14116x10 ⁰	-0.10316x10 ⁻³	-0.19748x10 ⁻⁴	0.94485x10 ⁻¹
	C ⁺	-0.13941x10 ⁻³	0.80675x10 ⁻⁶	-0.32224x10 ⁻⁸	0.30977x10 ⁻⁴
CaSO ₄	B ⁽⁰⁾	0.12004x10 ⁻²	-0.10826x10 ⁻⁴	0.48239x10 ⁻⁷	-0.17922x10 ⁻²
	B ⁽¹⁾	0.12505x10 ⁻¹	-0.49188x10 ⁻⁴	0.29291x10 ⁻⁶	-0.18739x10 ⁻¹
	B ⁽²⁾	-0.14116x10 ⁰	-0.10316x10 ⁻³	-0.19748x10 ⁻⁴	0.94485x10 ⁻¹
	C ⁺	0.0	0.0	0.0	0.0
SrSO ₄	B ⁽⁰⁾	0.12004x10 ⁻²	-0.10826x10 ⁻⁴	0.48239x10 ⁻⁷	-0.17922x10 ⁻²
	B ⁽¹⁾	0.12505x10 ⁻¹	-0.49188x10 ⁻⁴	0.29291x10 ⁻⁶	-0.18739x10 ⁻¹
	B ⁽²⁾	-0.14116x10 ⁰	-0.10316x10 ⁻³	-0.19748x10 ⁻⁴	0.94485x10 ⁻¹
	C ⁺	-0.13941x10 ⁻³	0.80675x10 ⁻⁶	-0.32224x10 ⁻⁸	0.30977x10 ⁻⁴
NaOH	B ⁽⁰⁾	0.85391x10 ⁻³	-0.10023x10 ⁻⁴	0.26696x10 ⁻⁷	-0.75941x10 ⁻³
	B ⁽¹⁾	0.13036x10 ⁻²	0.70706x10 ⁻⁵	-0.22250x10 ⁻⁷	0.38312x10 ⁻²
	C ⁺	-0.13484x10 ⁻³	0.86211x10 ⁻⁶	-0.19111x10 ⁻⁸	0.26884x10 ⁻⁴

APPENDIX 2

**THERMODYNAMIC DATA FOR THE
MINERAL DISSOCIATION AND SPECIES ASSOCIATION REACTIONS
AT 25°C AND TO 200°C.**

Table A.9: Elements in the *PHREEQEX* data base and their thermodynamic properties.

no.	species	ΔG_f° (kcal/mol)	ΔH_f°	S° (cal/mol·K)	C_p°	ref. ¹
1	H ⁺	0.00	0.00	0.00	0.00	W
2	e ⁻	0.00	0.00	0.00	0.00	W
3	H ₂ O	-56.687	-68.315	16.715	17.995	W
4	Ca ⁺²	-132.30	-129.74	-12.70	-----	W
5	Mg ⁺²	-108.70	-111.58	-33.00	-----	W
6	Na ⁺	-62.593	-57.39	14.10	11.10	W
7	K ⁺	-67.70	-60.32	24.50	5.20	W
8	Fe ⁺²	-18.50	-21.30	-32.90	-----	W
9	Mn ⁺²	-54.50	-52.76	-17.60	12.00	W
10	Al ⁺³	-116.00	-127.00	-76.90	-----	W
11	Ba ⁺²	-134.02	-128.50	2.30	-----	W
12	Sr ⁺²	-133.71	-130.30	-7.78	-----	W
13	H ₄ SiO ₄ ⁰	-314.70	-350.45	43.00	-----	W
14	Cl ⁻	-31.372	-39.952	13.50	-32.60	W
15	CO ₃ ⁻²	-126.17	-161.84	-13.60	-----	W
16	SO ₄ ⁻²	-177.97	-217.32	4.80	-70.00	W
17	NO ₃ ⁻	-26.00	-49.00	35.00	-20.70	W
18	H ₃ BO ₃ ⁰	-231.56	-256.29	38.80	-----	W
19	PO ₄ ⁻³	-243.50	-305.30	-53.00	-----	W
20	F ⁻	-66.64	-79.50	-3.30	-25.50	W
21	Li ⁺	-70.10	-66.56	3.20	16.40	W
22	Br ⁻	-24.85	-29.05	19.70	-33.90	W
23	Ni ⁺²	-10.90	-12.90	-30.80	-----	W
24	Co ⁺²	-13.00	-13.90	-27.00	-----	W
25	Cu ⁺²	15.66	15.48	-23.80	-----	W
26	Rb ⁺	-60.03	-67.87	29.04	-----	W
27	I ⁻	-12.33	-13.19	26.60	-34.00	W
28	Cs ⁺	-69.79	-61.73	31.80	-2.50	W
29	Be ⁺²	-90.75	-91.50	-31.00	-----	W
30	Ra ⁺²	-134.20	-126.00	13.00	-----	W

1. W: Wagman, D.D., W.H. Evans, V.B. Parker, R.H. Schumm, I. Harlow, S.M. Bailey, K.L. Churney and R.L. Nuttal, 1982, The N.B.S. tables of chemical thermodynamic properties: selected values for inorganic and C₁ and C₂ organic substances in S.I. units, *Journal of Physical and Chemical Reference Data (Supplement 2)*, 11:1-392.

Table A.10: Values of $\log K_{eq}$ and ΔH_R^0 at 25°C for the association reactions of the species in the PHREEQEX data base.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R^0 value ²	at 25°C ref. ³	high temperature regression function ¹ ref. ³
31	OH ⁻	-14.000	W	13.35	W	W
32	S ₂ ⁻²	57.582	W	-104.68	W	----
33	S ₃ ⁻²	94.363	W	-161.62	W	----
34	S ₄ ⁻²	130.924	W	-218.26	W	----
35	S ₅ ⁻²	167.266	W	-274.60	W	----
36	SO ₂ ⁰	5.333	W	3.50	W	----
37	S ₄ O ₆ ⁻²	76.006	W	-106.47	W	W
38	SO ₃ ⁻²	-3.653	W	-2.90	W	----
39	HSO ₃ ⁻	3.568	W	-0.67	W	----
40	H ₂ SO ₃ ⁰	5.334	W	3.495	W	----
41	HSO ₄ ⁻	1.994	W	5.24	W	W
42	S ⁻²	20.728	W	-48.04	W	----
43	HS ⁻	33.644	W	-60.14	W	----
44	H ₂ S ⁰	40.637	W	-65.44	W	----
45	S ₂ O ₈ ⁻²	-65.560	W	113.24	W	----
46	S ₂ O ₃ ⁻²	38.406	W	-61.94	W	----
47	S ₂ O ₄ ⁻²	10.488	W	-18.72	W	----
48	AlOH ⁺²	-4.975	W	11.90	B	K
49	Al(OH) ₂ ⁺	-9.300	B	----		K
50	Al(OH) ₃ ⁰	-15.000	B	----		----
51	Al(OH) ₄ ⁻	-22.539	W	41.15	W	K
52	Al ₂ (OH) ₂ ⁺⁴	-7.700	B	----		----
53	Al ₃ (OH) ₄ ⁺⁵	-13.940	B	----		----
54	AlO ₂ ⁻	-22.558	W	41.13	W	----
55	AlF ⁺²	6.861	W	----		----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25° ref. ³	temp. reg. func. ¹ ref. ³
56	AlF_2^+	12.256	W	20.00	P	----
57	AlF_3^0	16.185	W	2.50	W	----
58	AlF_4^-	19.720	P	----		----
59	$AlSO_4^+$	3.020	K	2.15	P	K
60	$Al(SO_4)_2^-$	4.920	P	2.84	P	----
61	$Al_{13}O_4(OH)_{24}^{+7}$	-98.730	B	----		----
62	$B(OH)_4^-$	-9.234	W	3.37	W	----
63	$H_2BO_3^-$	-9.240	P	3.22	P	----
64	$BF(OH)_3^-$	-0.400	P	1.85	P	----
65	$BF_2(OH)_2^-$	9.050	W	1.64	P	----
66	BF_3OH^-	14.656	W	-6.84	W	----
67	BF_4^-	20.041	W	-7.06	W	----
68	$B_4O_7^{2-}$	-14.810	W	----		----
69	$HB_4O_7^-$	-0.737	W	----		----
70	$H_2B_4O_7^0$	5.347	W	----		----
71	BO_2^-	-9.238	W	3.37	W	----
72	$B_2O(OH)_5^-$	-9.360	B	----		----
73	$B_3O_3(OH)_4^-$	-7.030	B	----		----
74	$B_4O_5(OH)_4^{2-}$	-16.300	B	----		----
75	$BaOH^+$	-11.807	W	15.10	P	K
76	$BaSO_4^0$	2.310	K	----		K
77	$BaCO_3^0$	2.500	K	----		K
78	$BaHCO_3^+$	11.770	K	----		K
79	BaF^+	0.330		----		----
80	$BaNO_3^+$	-0.938	W	2.26	W	----
81	$BeOH^+$	-5.400	B	----		----
82	$Be(OH)_2^0$	-13.650	B	----		----
83	$Be(OH)_3^-$	-23.250	B	----		----
84	$Be(OH)_4^{2-}$	-37.410	B	----		----
85	Be_2OH^{+3}	-3.970	B	5.00	B	----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25° ref. ³	temp. reg. func. ¹ ref. ³
86	$\text{Be}_3(\text{OH})_3^{+3}$	-8.584	W	16.00	B	----
87	$\text{Be}_6(\text{OH})_8^{+4}$	-27.200	B	----		----
88	BeO_2^{-2}	-37.474	W	39.13	W	----
90	HCO_3^-	10.330	K	-3.55	W	K
91	H_2CO_3^0	16.700	K	-5.38	W	K
92	CO_2^0	16.696	W	-5.35	W	----
93	CO^0	11.541	W	-3.70	W	----
94	HCO_2^-	10.560	W	-8.19	W	----
95	HCO_2H^0	14.292	W	-8.16	W	----
96	CH_4^0	38.191	W	-64.39	W	----
97	CH_3OH^0	21.334	W	-33.57	W	----
98	CH_3Cl^0	18.193	W	-27.46	W	----
99	CH_3NH_2^0	133.688	W	-215.26	W	----
100	CaCl_2^0	-0.123		-209.82		----
101	$\text{Ca}(\text{OH})_2^0$	-28.000		26.65		----
102	CaOH^+	-12.672	W	14.54	P	K
103	CaCO_3^0	3.140	K	4.02	P	K
104	CaHCO_3^+	11.350	K	1.81	P	K
105	CaSO_4^0	-2.300	K	1.47	P	K
106	CaPO_4^-	6.459	P	3.10	P	----
107	CaHPO_4^0	15.085	P	-0.23	P	----
108	$\text{CaH}_2\text{PO}_4^+$	20.961	P	-1.12	P	----
109	CaF^+	0.940	P	3.80	P	----
110	HCl^0	-6.100	T	18.63	T	----
111	HF^0	3.159	W	3.00	W	----
112	HF_2^-	3.592	W	3.66	W	----
115	KCl^0	-2.010	K	----		K
116	KCO_3^-	1.075	K	----		K
117	KSO_4^-	0.748	W	1.01	W	K
118	KOH^0	-14.452	B	----		----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25° ref. ³	temp. reg. func. ¹ ref. ³
119	$KS_2O_8^-$	-64.681	W	114.86	W	-----
120	$KP_2O_7^3$	23.110	W	1.23	W	-----
121	$KHPO_4^-$	12.636	P	-3.53	P	-----
122	$LiSO_4^-$	0.755	W	-0.72	W	-----
123	$LiOH^0$	-13.991	W	13.38	W	-----
124	$LiNO_3^0$	0.359	W	0.02	W	-----
125	$LiHPO_4^-$	13.561	W	2.36	W	-----
126	$LiP_2O_7^3$	24.400	W	0.54	W	-----
127	$LiHP_2O_7^2$	32.096	W	-1.16	W	-----
130	$Mg_4(OH)^{+4}_4$	-39.710	B	-----		-----
131	$MgPO_4^-$	6.589	P	3.10	P	-----
132	$MgHPO_4^0$	15.216	P	-0.23	P	-----
133	$MgH_2PO_4^+$	21.066	P	-1.12	P	-----
134	MgF^+	1.820	K	4.67	P	-----
135	$MgOH^+$	-11.425	W	-----		K
136	$MgCO_3^0$	2.980	K	2.71	P	K
137	$MgHCO_3^+$	11.310	W	-2.53	P	K
138	$MgSO_4^0$	2.250	W	4.80	W	K
139	$MgP_2O_7^2$	27.991	W	2.37	W	-----
140	FeO_2^-	-45.186	W	-----		-----
141	$HFeO_2^-$	-30.731	W	-----		-----
142	FeI^{+2}	-11.127	W	-----		-----
143	$FeNO^{+2}$	35.268	W	-67.97	W	-----
144	FeN_3^{+2}	246.294	W	-392.26	W	-----
145	$FeNO_3^{+2}$	-11.992	W	-----		-----
146	$FeBr^{+2}$	-12.388	W	15.75	W	-----
147	$FeOH^+$	-6.771	W	12.02	W	-----
148	$Fe(OH)_2^0$	-20.570	B	28.57	B	-----
149	$Fe(OH)_3^-$	-30.721	W	30.30	B	-----
150	$Fe(OH)_4^2$	-45.152	W	-----		-----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25°C ref. ³	temp. reg. func. ¹ ref. ³
151	FeCl ⁺	-0.530	K	-----		K
152	FeCl ₂ ⁰	-8.210	K	-----		K
153	FeF ⁺	-0.740		-----		-----
154	FeSO ₄ ⁰	2.250	P	3.23	P	-----
155	Fe(HS) ₂ ⁰	76.250	P	-120.28	P	-----
156	Fe(HS) ₃ ⁻	111.937	P	-180.42	P	-----
157	FeHPO ₄ ⁰	15.946	P	-3.53	P	-----
158	FeH ₂ PO ₄ ⁺	22.253	P	-4.52	P	-----
159	Fe ⁺³	-13.011	W	9.70	W	-----
160	FeOH ⁺²	-15.178	W	20.12	W	-----
161	Fe(OH) ₂ ⁺	-20.175	W	10.00	P	-----
162	Fe(OH) ₃ ⁰	-22.951	W	10.00	P	-----
163	Fe(OH) ₄ ⁻	-34.630	P	10.00	P	-----
164	Fe ₂ (OH) ₂ ⁺⁴	-28.876	W	32.93	W	-----
165	Fe ₃ (OH) ₄ ⁺⁵	-45.400	P	44.30	P	-----
166	FeCl ⁺²	-11.590	W	18.15	W	-----
167	FeCl ₂ ⁺	-10.903	W	10.00	P	-----
168	FeCl ₃ ⁰	-11.923	W	10.00	P	-----
169	FeCl ₄ ⁻	-13.800	K	-----		K
170	FeSO ₄ ⁺	-8.884	W	15.92	W	-----
171	Fe(SO ₄) ₂ ⁻	-7.616	W	14.60	P	-----
172	FeHPO ₄ ⁺	4.740	P	12.23	P	-----
173	FeH ₂ PO ₄ ⁺²	11.950	P	5.48	P	-----
174	FeF ⁺²	-6.150	W	12.10	W	-----
175	FeF ₂ ⁺	-1.415	W	13.90	W	-----
176	FeF ₃ ⁰	0.970	P	15.40	P	-----
180	MnOH ⁺	-10.546	W	13.38	W	-----
181	Mn(OH) ₂ ⁰	-22.200	B	-----		-----
182	Mn(OH) ₃ ⁻	-34.203	W	-----		-----
183	Mn(OH) ₄ ⁻²	-48.300	B	-----		-----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25°C ref. ³	temp. reg. func. ¹ ref. ³
184	$Mn_2(OH)^{+3}$	-10.560	B	-----		-----
185	$Mn_2(OH)_3^+$	-23.900	B	-----		-----
186	$MnCl^+$	0.614	W	-----		-----
187	$MnCl_2^0$	0.276	W	-----		-----
188	$MnCl_3$	-0.283	W	-----		-----
189	$MnCl_4^{2-}$	-0.080	K	-----		-----
190	$MnCO_3^0$	6.500	K	-----		K
191	$MnHCO_3^+$	11.237	W	-3.60	P	-----
192	$MnSO_4^0$	2.294	W	3.38	W	-----
193	MnF^+	0.850	W	-----		-----
194	Mn^{+3}	-25.507	P	25.76	P	-----
195	MnO_4^{2-}	-118.416	W	170.02	W	-----
196	$HMnO_2$	-34.440	T	-----		-----
197	MnO_4^-	-127.799	W	196.62	W	W
198	$Mn(NO_3)_2^0$	0.600	P	-0.40	P	-----
200	HNO_3^0	-1.430	K	-----		K
201	NO_2^-	28.138	W	-44.32	W	W
202	HNO_2^0	30.916	W	-47.26	W	-----
203	N_2^0	207.080	P	-312.13	P	-----
204	NH_3^0	109.806	W	-174.58	W	-----
205	NH_4^+	119.503	W	-187.62	W	W
206	NH_4SO_4	120.190	P	-187.06	P	-----
207	N_3	254.467	W	-400.40	W	-----
208	N_3H^0	259.085	W	-403.99	W	-----
209	NH_4OH^0	109.808	W	-174.58	W	-----
210	$N_2H_4^0$	187.872	W	-302.57	W	-----
211	$N_2H_5^+$	196.756	W	-313.69	W	W
212	$N_2H_5OH^0$	188.776	W	-303.69	W	W
215	$NaCl^0$	-0.850	K	-----		K
216	$NaOH^0$	-14.177	B	-112.36	B	-----

Table A.10: continued.

species no.	species	$\log K_{eq}$ value	at 25°C ref. ³	ΔH_R° value ²	at 25° ref. ³	temp. reg. func. ¹ ref. ³
217	NaCO ₃ ⁻	0.533	W	-4.46	W	K
218	Na ₂ CO ₃ ⁰	-0.670	K	-----		K
219	NaHCO ₃ ⁰	10.502	W	-6.37	W	K
220	NaSO ₄ ⁻	0.723	W	1.12	W	K
221	Na ₂ SO ₄ ⁰	1.510	K	-2.64	T	K
222	NaF ⁰	-0.870		-----		-----
223	NaHPO ₄ ⁻	12.636	P	-3.53	P	-----
224	NaS ₂ O ₃ ⁻	39.034	W	-61.78	W	-----
225	NaHP ₂ O ₇ ⁻²	28.583	W	-----		-----
226	Na ₂ P ₂ O ₇ ⁻²	23.237	W	-----		-----
228	HPO ₄ ⁻²	12.344	W	-3.53	W	-----
229	H ₂ PO ₄ ⁻	19.549	W	-4.52	W	-----
230	H ₃ PO ₄ ⁰	21.697	W	-2.62	W	-----
231	P ₂ O ₇ ⁻⁴	20.808	W	-0.52	W	-----
232	HP ₂ O ₇ ⁻³	30.117	W	-1.42	W	-----
233	H ₂ P ₂ O ₇ ⁻²	36.788	W	-2.32	W	-----
234	H ₃ P ₂ O ₇ ⁻	39.060	W	-1.82	W	-----
235	H ₄ P ₂ O ₇ ⁰	40.599	W	0.09	W	-----
236	H ₃ SiO ₄ ⁻	-9.929	K	8.94	P	K
237	H ₂ SiO ₄ ⁻²	-21.617	P	29.72	P	-----
238	SiF ₆ ⁻²	27.787	W	-16.26	W	-----
239	H ₂ SiO ₃ ⁰	-0.010	W	-0.02	W	-----
240	HSi(OH) ₆ ⁻	-9.877	W	-----		-----
241	H ₂ Si(OH) ₆ ⁰	0.019	W	0.03	W	-----
242	Si ₄ O ₆ (OH) ₆ ⁻²	-13.440	B	-----		-----
243	Si ₄ O ₈ (OH) ₄ ⁻⁴	-35.800	B	-----		-----
244	SrOH ⁺	-13.192	W	14.50	P	K
245	SrSO ₄ ⁰	2.200	K	1.60	T	K
246	SrF ⁺	0.840		-----		-----
247	SrCO ₃ ⁰	2.850	K	-----		K

Table A.10: continued.

species no.	species	$\log K_{eq}$ at 25°C value ref. ³	ΔH_R° at 25° value ² ref. ³	temp. reg. func. ¹ ref. ³
248	SrHCO_3^+	11.590 K	-----	K
249	O_2^0	-86.080 P	134.79 P	-----
250	H_2^0	-3.086 W	-1.00 W	-----

1: see Table A.11 for the regression coefficients for the regression function.

2: values of ΔH_R° are in kcal/mol.

3: references are as follows:

P: Parkhurst, D.L., D.C. Thorstenson and L.N. Plummer, 1980, PHREEQE - a computer program for geochemical calculations, *U.S.G.S. Water Resources Investigations* 80-96, 210pp.

K: Kharaka, Y.K. and I. Barnes, 1973, SOLMNEQ: solution - mineral equilibrium computations, *NTIS, Report PB214-899*, 82pp.

T: Truesdell, A.H. and B.F. Jones, 1974, WATEQ, a computer program for calculating chemical equilibria of natural waters, *Journal of Research, U.S.G.S.*, 2:233-248.

Plummer, L.N., B.F. Jones and A.H. Truesdell, 1976, WATEQF - A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibria of natural waters, *U.S.G.S. Water Resources Investigations* 76-13, 70pp.

B: Baes, C.F., Jr. and R.E. Mesmer, 1976, The hydrolysis of cations, A Wiley Interscience Publication, John Wiley and Sons, Inc., 489pp.

W: Wagman, D.D., W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, 1968, Selected values of chemical thermodynamic properties: Tables for the first thirty-five elements in the standard order of arrangement, *U.S. National Bureau of Standards Technical Note* 270-3, 270pp.

Wagman, D.D., W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, 1969, Selected values of chemical thermodynamic properties: Tables for elements 35 through 53 in the standard order of arrangement, *U.S. National Bureau of Standards Technical Note* 270-4, 141pp.

Wagman, D.D., W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey, R.H. Schumm and K.L. Churney, 1971, Selected values of chemical thermodynamic properties: Tables for elements 54 through 61 in the standard order of arrangement, *U.S. National Bureau of Standards Technical Note 270-5*, 37pp.

Parker, V.B., D.D. Wagman, and W.H. Evans, 1971, Selected values of chemical thermodynamic properties: Tables for alkaline earth elements (elements 92 through 97) in the standard order of arrangement, *U.S. National Bureau of Standards Technical Note 270-6*, 106pp.

Schumm, R.H., D.D. Wagman, S.M. Bailey, W.H. Evans, V.B. Parker, 1973, Selected values of chemical thermodynamic properties: Tables for the lanthanide (rare earth) elements, (elements 62 through 76) in the standard order of arrangement, *U.S. National Bureau of Standards Technical Note 270-7*, 75pp.

Wagman, D.D., W.H. Evans, V.B. Parker, R.H. Schumm and R.L. Nuttal, 1981, Selected values of chemical thermodynamic properties: Compounds of uranium, protactinium, thorium, actinium and the alkali metals, *U.S. National Bureau of Standards Technical Note 270-8*, 134 pp.

Wagman, D.D., W.H. Evans, V.B. Parker, R.H. Schumm, I. Harlow, S.M. Bailey, K.L. Churney and R.L. Nuttal, 1982, The N.B.S. tables of chemical thermodynamic properties: selected values for inorganic and C₁ and C₂ organic substances in S.I. units, *Journal of Physical and Chemical Reference Data (Supplement 2)*, 11:1-392.

Table A.11: Coefficients for the equation that interpolates $\log K_{eq}$ of the association reaction of the species in the *PHREEQEX* data base to 200°C.

no.	species	interpolation coefficients ¹					ref. ²
		a_1	a_2	a_3	a_4	a_5	
31	OH ⁻	$0.31309 \times 10^{+1}$	-0.17354×10^{-1}	$-0.31379 \times 10^{+4}$	0.43711×10^{-5}	$-0.16138 \times 10^{+6}$	W
37	S ₄ O ₆ ²⁻	$-0.70293 \times 10^{+2}$	0.16273×10^0	$-0.26476 \times 10^{+5}$	-0.49918×10^{-4}	$0.11928 \times 10^{+7}$	W
41	HSO ₄ ⁻	$0.24247 \times 10^{+1}$	-0.19201×10^{-1}	$0.66686 \times 10^{+3}$	0.63664×10^{-5}	$-0.13305 \times 10^{+6}$	W
48	AlOH ⁺	$-0.16784 \times 10^{+2}$	0.39647×10^{-1}	$0.23018 \times 10^{+4}$	-0.30456×10^{-4}	$-0.44542 \times 10^{+6}$	K
49	Al(OH) ₂ ⁺	$-0.37734 \times 10^{+2}$	0.56363×10^{-1}	$0.73977 \times 10^{+4}$	0.28109×10^{-5}	$-0.12502 \times 10^{+7}$	K
51	Al(OH) ₃ ⁰	$-0.18835 \times 10^{+3}$	0.40540×10^0	$0.33233 \times 10^{+5}$	-0.31478×10^{-3}	$-0.34902 \times 10^{+7}$	K
59	AlSO ₄ ⁺	$0.75044 \times 10^{+1}$	-0.10664×10^{-1}	$-0.14486 \times 10^{+4}$	0.19883×10^{-4}	$0.15725 \times 10^{+6}$	K
75	BaOH ⁺	$-0.30631 \times 10^{+2}$	0.53953×10^{-1}	$0.33293 \times 10^{+4}$	-0.38994×10^{-4}	$-0.58907 \times 10^{+6}$	K
76	BaSO ₄ ⁰	$0.21058 \times 10^{+2}$	-0.40268×10^{-1}	$-0.42485 \times 10^{+4}$	0.33801×10^{-4}	$0.40018 \times 10^{+6}$	K
77	BaCO ₃ ⁰	$-0.81309 \times 10^{+2}$	0.14793×10^0	$0.20203 \times 10^{+5}$	-0.88257×10^{-4}	$-0.17964 \times 10^{+7}$	K
78	BaHCO ₃ ⁺	$0.11854 \times 10^{+3}$	-0.20866×10^0	$-0.26149 \times 10^{+5}$	0.17318×10^{-3}	$0.24668 \times 10^{+7}$	K
90	HCO ₃ ⁻	$0.52765 \times 10^{+2}$	-0.84967×10^{-1}	$-0.10959 \times 10^{+5}$	0.71610×10^{-4}	$0.11811 \times 10^{+7}$	K
91	H ₂ CO ₃ ⁰	$0.52294 \times 10^{+2}$	-0.74445×10^{-1}	$-0.10506 \times 10^{+5}$	0.75835×10^{-4}	$0.13419 \times 10^{+7}$	K
102	CaOH ⁺	$-0.18163 \times 10^{+2}$	0.32886×10^{-1}	$0.46991 \times 10^{+3}$	-0.25212×10^{-4}	$-0.34094 \times 10^{+6}$	K
103	CaCO ₃ ⁰	$0.16244 \times 10^{+2}$	-0.26702×10^{-1}	$-0.35512 \times 10^{+4}$	0.35257×10^{-4}	$0.32304 \times 10^{+6}$	K
104	CaHCO ₃ ⁺	$0.60388 \times 10^{+2}$	-0.88734×10^{-1}	$-0.13297 \times 10^{+5}$	0.77102×10^{-4}	$0.13479 \times 10^{+7}$	K
105	CaSO ₄ ⁰	$0.84883 \times 10^{+2}$	-0.15017×10^0	$-0.20813 \times 10^{+5}$	0.11164×10^{-3}	$0.19623 \times 10^{+7}$	K
115	KCl ⁰	$-0.97026 \times 10^{+2}$	0.16944×10^0	$0.23416 \times 10^{+5}$	-0.10459×10^{-3}	$-0.21994 \times 10^{+7}$	K
116	KCO ₃ ⁻	$-0.48397 \times 10^{+3}$	0.91511×10^0	$0.11200 \times 10^{+6}$	-0.62965×10^{-3}	$-0.95502 \times 10^{+7}$	K
117	KSO ₄ ⁻	$0.83333 \times 10^{+1}$	-0.15065×10^{-1}	$-0.21919 \times 10^{+4}$	0.18139×10^{-4}	$0.24791 \times 10^{+6}$	K
135	MgOH ⁺	$-0.48142 \times 10^{+2}$	0.93291×10^{-1}	$0.72988 \times 10^{+4}$	-0.66280×10^{-4}	$-0.85858 \times 10^{+6}$	K
136	MgCO ₃ ⁰	$0.36621 \times 10^{+1}$	-0.29832×10^{-2}	$-0.61200 \times 10^{+3}$	0.13491×10^{-4}	$0.93871 \times 10^{+5}$	K
137	MgHCO ₃ ⁺	$0.35467 \times 10^{+2}$	-0.52215×10^{-1}	$-0.67142 \times 10^{+4}$	0.54850×10^{-4}	$0.81275 \times 10^{+6}$	K
138	MgSO ₄ ⁰	$-0.11739 \times 10^{+2}$	0.30147×10^{-1}	$0.24341 \times 10^{+4}$	-0.16724×10^{-4}	$-0.13569 \times 10^{+6}$	K
151	FeCl ⁺	$-0.13697 \times 10^{+3}$	0.25109×10^0	$0.33443 \times 10^{+5}$	-0.16349×10^{-3}	$-0.32028 \times 10^{+7}$	K
152	FeCl ₂ ⁰	$-0.19897 \times 10^{+2}$	0.39200×10^{-1}	0.17048×10^{-3}	-0.89689×10^{-12}	-0.15042×10^{-1}	K
154	FeSO ₄ ⁰	$0.13557 \times 10^{+2}$	-0.28418×10^{-1}	$-0.22421 \times 10^{+4}$	0.31215×10^{-4}	$0.18612 \times 10^{+6}$	K
169	FeCl ₃ ⁰	$-0.21399 \times 10^{+2}$	0.12875×10^{-1}	$0.20256 \times 10^{+4}$	0.40366×10^{-5}	$-0.30153 \times 10^{+6}$	K

Table A.11: continued.

no.	species	regression coefficients ¹					ref. ²
		a ₁	a ₂	a ₃	a ₄	a ₅	
190	MnCO ₃ ⁰	0.45329x10 ⁺¹	-0.99773x10 ⁻²	0.79852x10 ⁺³	0.24131x10 ⁻⁴	0.10387x10 ⁺⁵	K
196	MnO ₄ ⁻	-0.57049x10 ⁺¹	0.42392x10 ⁻²	-0.33915x10 ⁺⁵	-0.18150x10 ⁻⁴	-0.71049x10 ⁺⁶	W
200	HNO ₃ ⁰	0.11862x10 ⁺²	-0.20420x10 ⁻¹	-0.40395x10 ⁺⁴	0.23165x10 ⁻⁴	0.38097x10 ⁺⁶	K
201	NO ₂ ⁻	0.10173x10 ⁺¹	-0.10529x10 ⁻²	0.77409x10 ⁺⁴	0.30576x10 ⁻⁵	0.10663x10 ⁺⁶	W
205	NH ₄ ⁺	0.68823x10 ⁺¹	-0.70477x10 ⁻²	0.31437x10 ⁺⁵	0.18640x10 ⁻⁴	0.67771x10 ⁺⁶	W
211	N ₂ H ₅ ⁺	0.70716x10 ⁺¹	-0.28651x10 ⁻²	0.52425x10 ⁺⁵	0.26364x10 ⁻⁴	0.10986x10 ⁺⁷	W
212	N ₂ H ₅ OH ⁰	0.11421x10 ⁺²	-0.12149x10 ⁻¹	0.49511x10 ⁺⁵	0.30296x10 ⁻⁴	0.10863x10 ⁺⁷	W
215	NaCl ⁰	-0.45559x10 ⁺²	0.64100x10 ⁻¹	0.12747x10 ⁺⁵	-0.26744x10 ⁻⁴	-0.13146x10 ⁺⁷	K
217	NaCO ₃ ⁻	-0.11458x10 ⁺³	0.22472x10 ⁰	0.25824x10 ⁺⁵	-0.13911x10 ⁻³	-0.22572x10 ⁺⁷	K
218	Na ₂ CO ₃ ⁰	-0.15554x10 ⁺³	0.26798x10 ⁰	0.38597x10 ⁺⁵	-0.15803x10 ⁻³	-0.35942x10 ⁺⁷	K
219	NaHCO ₃ ⁰	0.80477x10 ⁺²	-0.14099x10 ⁰	-0.17145x10 ⁺⁵	0.11818x10 ⁻³	0.16566x10 ⁺⁷	K
220	NaSO ₄ ⁻	-0.62120x10 ⁺¹	0.15316x10 ⁻¹	0.13690x10 ⁺⁴	-0.10714x10 ⁻⁴	-0.15695x10 ⁺⁶	K
221	Na ₂ SO ₄ ⁰	0.73356x10 ⁺¹	-0.13982x10 ⁻¹	-0.13222x10 ⁺⁴	0.93863x10 ⁻⁵	0.17270x10 ⁺⁶	K
236	H ₃ SiO ₄ ⁻	0.60599x10 ⁺²	-0.98378x10 ⁻¹	-0.12909x10 ⁺⁵	0.70850x10 ⁻⁴	0.13823x10 ⁺⁷	K
244	SrOH ⁺	-0.66783x10 ⁺²	0.12086x10 ⁰	0.12002x10 ⁺⁵	-0.84469x10 ⁻⁴	-0.13608x10 ⁺⁷	K
245	SrSO ₄ ⁰	-0.83459x10 ⁺¹	0.10955x10 ⁻¹	0.30043x10 ⁺⁴	0.62289x10 ⁻⁵	-0.29771x10 ⁺⁶	K
247	SrCO ₃ ⁰	-0.48592x10 ⁺²	0.83073x10 ⁻¹	0.13372x10 ⁺⁵	-0.41166x10 ⁻⁴	-0.12895x10 ⁺⁷	K
248	SrHCO ₃ ⁺	0.42259x10 ⁺²	-0.71778x10 ⁻¹	-0.76748x10 ⁺⁴	0.86636x10 ⁻⁴	0.77973x10 ⁺⁶	K

1: regression equation is: $\log K_{eq}(T) = a_1 + a_2 \cdot T + a_3 \frac{1}{T} + a_4 \cdot T^2 + a_5 \frac{1}{T^2}$

where temperature is in degrees K.

2: source of data for calculating the regression coefficients is as follows:

W: based upon a regression of $\log K_{eq}$ values calculated at high temperatures with the heat capacities of the species obtained from Wagman et al. (1968, 1969, 1971, 1981, 1982), Parker et al. (1971) and Schumm et al. (1973) (see Table A.10 for references)

K: based upon a regression of $\log K_{eq}$ values from Kharaka and Barnes (1973) (see Table A.10 for reference)

Table A.12: Values of $\log K_{eq}$ at 25°C for the dissociation reactions of the minerals in the *PHREEQEX* or *PHREEQEP* data bases.

mineral	chemical formula	$\log K_{eq}$	ref. ¹
CARBONATES			
Calcite	CaCO_3	-8.48	H
Aragonite	CaCO_3	-8.30	K
Magnesite	MgCO_3	-8.20	H
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	-17.00	H
Siderite	FeCO_3	-10.54	K
Strontianite	SrCO_3	-8.97	K
Witherite	BaCO_3	-7.63	K
Rhodochrosite	MnCO_3	-10.54	K
SULPHATES			
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.58	H
Anhydrite	CaSO_4	-4.39	H
Barite	BaSO_4	-9.96	K
Celestite	SrSO_4	-6.49	K
HALIDES			
Halite	NaCl	1.59	H
Sylvite	KCl	0.91	H
HYDROXIDES			
Gibbsite	$\text{Al}(\text{OH})_3$	-33.87	K
Brucite	$\text{Mg}(\text{OH})_2$	-11.47	H
Portlandite	$\text{Ca}(\text{OH})_2$	-5.42	H

Table A.12: continued.

mineral	chemical formula	$\log K_{eq}$	ref. ¹
<i>SILICATES</i>			
Quartz	SiO_2	-3.93	K
Albite (low)	$\text{NaAlSi}_3\text{O}_8$	3.11	K
Albite (high)	$\text{NaAlSi}_3\text{O}_8$	4.43	K
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	27.09	K
Microcline	KAlSi_3O_8	0.73	K
Fayalite	Fe_2SiO_4	19.43	K
Fosterite	Mg_2SiO_4	29.07	K
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	6.64	K
Laumontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	14.17	K
Wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	18.58	K
Kaolinite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4$	5.64	K
Dickite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4$	6.17	K
Halloysite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4$	8.91	K
Ca-Mont.	$\text{Ca}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	6.14	K
Mg-Mont.	$\text{Mg}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	6.04	K
Na-Mont.	$\text{Na}_{.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	6.12	K
K-Mont.	$\text{K}_{.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	5.86	K
Mg-Chlorite	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	59.02	K
Illite	$\text{K}_6\text{Mg}_{.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$	10.34	K

1: references are as follows:

H: Harvie, C.E., N. Mollar and J.H. Weare, 1984, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-H₂O system to high ionic strengths at 25°C, *Geochemica et Cosmochemica Acta*, 48:723-751.

K: Kharaka, Y.K. and I. Barnes, 1973, SOLMNEQ: solution-mineral equilibrium computations, *NTIS, Report PB214-899*, 82pp.

Table A.13: Coefficients for the equation that interpolates $\log K_{eq}$ of the mineral dissociation reaction to 200°C.

	interpolation coefficients ¹				
	a_1	a_2	a_3	a_4	a_5
Calcite	$-0.86486 \times 10^{+2}$	0.14498×10^0	$0.20207 \times 10^{+5}$	-0.12150×10^{-3}	$-0.19718 \times 10^{+7}$
Aragonite	$-0.68585 \times 10^{+2}$	0.11344×10^0	$0.15835 \times 10^{+5}$	-0.10053×10^{-3}	$-0.15737 \times 10^{+7}$
Magnesite	$-0.85678 \times 10^{+2}$	0.13798×10^0	$0.20092 \times 10^{+5}$	-0.11522×10^{-3}	$-0.18498 \times 10^{+7}$
Dolomite	$-0.11253 \times 10^{+3}$	0.18493×10^0	$0.25742 \times 10^{+5}$	-0.18967×10^{-3}	$-0.25858 \times 10^{+7}$
Siderite	$-0.87436 \times 10^{+2}$	0.13276×10^0	$0.20438 \times 10^{+5}$	-0.10311×10^{-3}	$-0.19620 \times 10^{+7}$
Strontianite	$-0.11572 \times 10^{+3}$	0.19882×10^0	$0.27039 \times 10^{+5}$	-0.15617×10^{-3}	$-0.26079 \times 10^{+7}$
Witherite	$0.61444 \times 10^{+3}$	$-0.11794 \times 10^{+1}$	$-0.14026 \times 10^{+6}$	0.79455×10^{-3}	$0.11491 \times 10^{+8}$
Rhodochrosite	$-0.94882 \times 10^{+2}$	0.15812×10^0	$0.21376 \times 10^{+5}$	-0.12845×10^{-3}	$-0.20519 \times 10^{+7}$
Gypsum	$-0.11156 \times 10^{+3}$	0.21179×10^0	$0.24712 \times 10^{+5}$	-0.16817×10^{-3}	$-0.21423 \times 10^{+7}$
Anhydrite	$0.51155 \times 10^{+2}$	-0.88167×10^{-1}	$-0.14373 \times 10^{+5}$	0.28752×10^{-4}	$0.14570 \times 10^{+7}$
Barite	$-0.12461 \times 10^{+3}$	0.22091×10^0	$0.29121 \times 10^{+5}$	-0.17267×10^{-3}	$-0.29816 \times 10^{+7}$
Celestite	$-0.89095 \times 10^{+2}$	0.15036×10^0	$0.21659 \times 10^{+5}$	-0.11873×10^{-3}	$-0.21614 \times 10^{+7}$
Halite	$-0.26334 \times 10^{+1}$	0.77680×10^{-2}	$0.17226 \times 10^{+4}$	-0.10108×10^{-4}	$-0.26418 \times 10^{+6}$
Sylvite	$-0.34563 \times 10^{+2}$	0.74235×10^{-1}	$0.86039 \times 10^{+4}$	-0.59890×10^{-4}	$-0.90613 \times 10^{+6}$
Gibbsite	$-0.17628 \times 10^{+3}$	0.29097×10^0	$0.34423 \times 10^{+5}$	-0.22046×10^{-3}	$-0.35741 \times 10^{+7}$
Brucite	$-0.17341 \times 10^{+3}$	0.30465×10^0	$0.39150 \times 10^{+5}$	-0.22521×10^{-3}	$-0.35715 \times 10^{+7}$
Portlandite	$-0.12416 \times 10^{+3}$	0.20898×10^0	$0.30378 \times 10^{+5}$	-0.15259×10^{-3}	$-0.28350 \times 10^{+7}$
Quartz	$0.11271 \times 10^{+2}$	-0.11785×10^{-1}	$-0.51868 \times 10^{+4}$	0.33975×10^{-5}	$0.48068 \times 10^{+6}$
Albite (low)	$-0.11962 \times 10^{+3}$	0.18445×10^0	$0.32856 \times 10^{+5}$	-0.11136×10^{-3}	$-0.28958 \times 10^{+7}$
Albite (high)	$-0.12682 \times 10^{+3}$	0.19607×10^0	$0.35073 \times 10^{+5}$	-0.11892×10^{-3}	$-0.30475 \times 10^{+7}$
Anorthite	$-0.33101 \times 10^{+2}$	0.60897×10^{-2}	$0.18239 \times 10^{+5}$	0.59740×10^{-5}	$-0.29732 \times 10^{+6}$
Microcline	$-0.10871 \times 10^{+3}$	0.16663×10^0	$0.29728 \times 10^{+5}$	-0.99810×10^{-4}	$-0.27630 \times 10^{+7}$
Fayalite	$-0.40171 \times 10^{+2}$	0.47209×10^{-1}	$0.17228 \times 10^{+5}$	-0.23534×10^{-4}	$-0.90472 \times 10^{+6}$
Fosterite	$-0.86803 \times 10^{+1}$	-0.10188×10^{-1}	$0.12326 \times 10^{+5}$	0.15700×10^{-4}	$-0.17443 \times 10^{+6}$
Analcime	$-0.64172 \times 10^{+2}$	0.88554×10^{-1}	$0.19334 \times 10^{+5}$	-0.47302×10^{-4}	$-0.14434 \times 10^{+7}$
Laumonite	$-0.11920 \times 10^{+3}$	0.15499×10^0	$0.37010 \times 10^{+5}$	-0.79663×10^{-4}	$-0.26582 \times 10^{+7}$
Wairakite	$-0.12440 \times 10^{+3}$	0.15750×10^0	$0.39974 \times 10^{+5}$	-0.86069×10^{-4}	$-0.27039 \times 10^{+7}$
Kaolinite	$-0.46302 \times 10^{+2}$	0.47092×10^{-1}	$0.13828 \times 10^{+5}$	-0.23100×10^{-4}	$-0.57201 \times 10^{+6}$

Table A.13: continued.

	regression coefficients				
	a_1	a_2	a_3	a_4	a_5
Dickite	$-0.61922 \times 10^{+2}$	0.76380×10^{-1}	$0.17692 \times 10^{+5}$	-0.43061×10^{-4}	$-0.90691 \times 10^{+6}$
Halloysite	$-0.50244 \times 10^{+2}$	0.52849×10^{-1}	$0.15964 \times 10^{+5}$	-0.26203×10^{-4}	$-0.69583 \times 10^{+6}$
Ca-Mont.	$0.51913 \times 10^{+2}$	-0.13658×10^0	$-0.10910 \times 10^{+5}$	0.98827×10^{-4}	$0.20223 \times 10^{+7}$
Mg-Mont.	$0.24660 \times 10^{+3}$	-0.49026×10^0	$-0.57902 \times 10^{+5}$	0.33559×10^{-3}	$0.62184 \times 10^{+7}$
Na-Mont.	$0.97010 \times 10^{+2}$	-0.21807×10^0	$-0.21688 \times 10^{+5}$	0.15513×10^{-3}	$0.29394 \times 10^{+7}$
K-Mont.	$0.52541 \times 10^{+2}$	-0.13485×10^0	$-0.11220 \times 10^{+5}$	0.97992×10^{-4}	$0.19944 \times 10^{+7}$
Mg-Chlorite	$0.17303 \times 10^{+3}$	-0.36810×10^0	$-0.27223 \times 10^{+5}$	0.27581×10^{-3}	$0.55559 \times 10^{+7}$
Illite	$0.51355 \times 10^{+2}$	-0.13084×10^0	$-0.98187 \times 10^{+4}$	0.95368×10^{-4}	$0.19949 \times 10^{+7}$

1: regression equation is: $\log K_{eq}(T) = a_1 + a_2 T + a_3 \frac{1}{T} + a_4 T^2 + a_5 \frac{1}{T^2}$
 where temperature is in degrees K.

references based upon a regression of $\log K_{eq}$ values from Kharaka and Barnes (1973)
 (see Table A.10 for reference)

Table A.14: Dissociation reactions for the minerals in the *PHREEQEX* and *PHREEQP* data bases.

mineral	reaction
Calcite	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{-2}$
Aragonite	$\text{CaCO}_3 = \text{Ca}^{+2} + \text{CO}_3^{-2}$
Magnesite	$\text{MgCO}_3 = \text{Mg}^{+2} + \text{CO}_3^{-2}$
Dolomite	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{+2} + \text{Mg}^{+2} + 2\text{CO}_3^{-2}$
Siderite	$\text{FeCO}_3 = \text{Fe}^{+2} + \text{CO}_3^{-2}$
Strontianite	$\text{SrCO}_3 = \text{Sr}^{+2} + \text{CO}_3^{-2}$
Witherite	$\text{BaCO}_3 = \text{Ba}^{+2} + \text{CO}_3^{-2}$
Rhodochrosite	$\text{MnCO}_3 = \text{Mn}^{+2} + \text{CO}_3^{-2}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$
Anhydrite	$\text{CaSO}_4 = \text{Ca}^{+2} + \text{SO}_4^{-2}$
Barite	$\text{BaSO}_4 = \text{Ba}^{+2} + \text{SO}_4^{-2}$
Celestite	$\text{SrSO}_4 = \text{Sr}^{+2} + \text{SO}_4^{-2}$
Halite	$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$
Sylvite	$\text{KCl} = \text{K}^+ + \text{Cl}^-$
Gibbsite	$\text{Al}(\text{OH})_3 = \text{Al}^{+3} + 3\text{OH}^-$
Brucite	$\text{Mg}(\text{OH})_2 = \text{Mg}^{+2} + 2\text{OH}^-$
Portlandite	$\text{Ca}(\text{OH})_2 = \text{Ca}^{+2} + \text{OH}^-$
Quartz	$\text{SiO}_2 = \text{H}_4\text{SiO}_4^0 - 2\text{H}_2\text{O}$
Albite (low)	$\text{NaAlSi}_3\text{O}_8 = 3\text{H}_4\text{SiO}_4^0 + \text{Na}^+ + \text{Al}^{+3} - 4\text{H}_2\text{O} - 4\text{H}^+$
Albite (high)	$\text{NaAlSi}_3\text{O}_8 = 3\text{H}_4\text{SiO}_4^0 + \text{Na}^+ + \text{Al}^{+3} - 4\text{H}_2\text{O} - 4\text{H}^+$
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8 = 2\text{H}_4\text{SiO}_4^0 + \text{Ca}^{+2} + 2\text{Al}^{+3} - 8\text{H}^+$
Microcline	$\text{KAlSi}_3\text{O}_8 = 3\text{H}_4\text{SiO}_4^0 + \text{K}^+ + \text{Al}^{+3} - 4\text{H}_2\text{O} - 4\text{H}^+$
Fayalite	$\text{Fe}_2\text{SiO}_4 = \text{H}_4\text{SiO}_4^0 + 2\text{Fe}^{+2} - 4\text{H}^+$
Fosterite	$\text{Mg}_2\text{SiO}_4 = \text{H}_4\text{SiO}_4^0 + 2\text{Mg}^{+2} - 4\text{H}^+$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O} = \text{Na}^+ + \text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 - 4\text{H}_2\text{O} - 4\text{H}^+$
Laumontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O} = \text{Ca}^{+2} + 2\text{Al}^{+3} + 4\text{H}_4\text{SiO}_4^0 - 8\text{H}^+$
Wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O} = \text{Ca}^{+2} + 2\text{Al}^{+3} + 4\text{H}_4\text{SiO}_4^0 - 2\text{H}_2\text{O} - 8\text{H}^+$
Kaolinite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4 = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O} - 6\text{H}^+$

Table A.14: continued.

mineral	reaction
Dickite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4 = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O} - 6\text{H}^+$
Halloysite	$\text{Al}_2\text{Si}_4\text{O}_5(\text{OH})_4 = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O} - 6\text{H}^+$
Illite	$\text{K}_{.6}\text{Mg}_{.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2 = .6\text{K}^+ + .25\text{Mg}^{+2} + 2.3\text{Al}^{+3} + 3.5\text{H}_4\text{SiO}_4^0 - 2\text{H}_2\text{O} - 8\text{H}^+$
Mg-Chlorite	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 = 5\text{Mg}^{+2} + 2\text{Al}^{+3} + 3\text{H}_4\text{SiO}_4^0 + 6\text{H}_2\text{O} - 16\text{H}^+$
Ca-Mont.	$\text{Ca}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 = .167\text{Ca}^{+2} + 2.33\text{Al}^{+3} + 3.67\text{H}_4\text{SiO}_4^0 - 2.678\text{H}_2\text{O} - 7.324\text{H}^+$
Mg-Mont.	$\text{Mg}_{.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 = .167\text{Mg}^{+2} + 2.33\text{Al}^{+3} + 3.67\text{H}_4\text{SiO}_4^0 - 2.678\text{H}_2\text{O} - 7.324\text{H}^+$
Na-Mont.	$\text{Na}_{.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 = .33\text{Na}^+ + 2.33\text{Al}^{+3} + 3.67\text{H}_4\text{SiO}_4^0 - 2.678\text{H}_2\text{O} - 7.324\text{H}^+$
K-Mont.	$\text{K}_{.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 = .33\text{K}^+ + 2.33\text{Al}^{+3} + 3.67\text{H}_4\text{SiO}_4^0 - 2.678\text{H}_2\text{O} - 7.324\text{H}^+$

Table A.15: Association reactions for the species in the *PHREEQEP* data base.

species	reaction
OH^-	$\text{H}_2\text{O} - \text{H}^+ = \text{OH}^-$
HCO_3^-	$\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$
CO_2^0	$\text{CO}_3^{2-} - \text{H}_2\text{O} + 2\text{H}^+ = \text{CO}_2^0$
CaCO_3^0	$\text{Ca}^{+2} + \text{CO}_3^{2-} = \text{CaCO}_3^0$
MgCO_3^0	$\text{Mg}^{+2} + \text{CO}_3^{2-} = \text{MgCO}_3^0$
HSO_4^-	$\text{SO}_4^{2-} + \text{H}^+ = \text{HSO}_4^-$
MgOH^+	$\text{Mg}^{+2} + \text{H}_2\text{O} - \text{H}^+ = \text{MgOH}^+$
$\text{Al}(\text{OH})^{+2}$	$\text{Al}^{+3} + \text{H}_2\text{O} - \text{H}^+ = \text{Al}(\text{OH})^{+2}$
$\text{Al}(\text{OH})_2^+$	$\text{Al}^{+3} + 2\text{H}_2\text{O} - 2\text{H}^+ = \text{Al}(\text{OH})_2^+$
$\text{Al}(\text{OH})_4^-$	$\text{Al}^{+3} + 4\text{H}_2\text{O} - 4\text{H}^+ = \text{Al}(\text{OH})_4^-$
H_3SiO_4^-	$\text{H}_4\text{SiO}_4^0 - \text{H}^+ = \text{H}_3\text{SiO}_4^-$

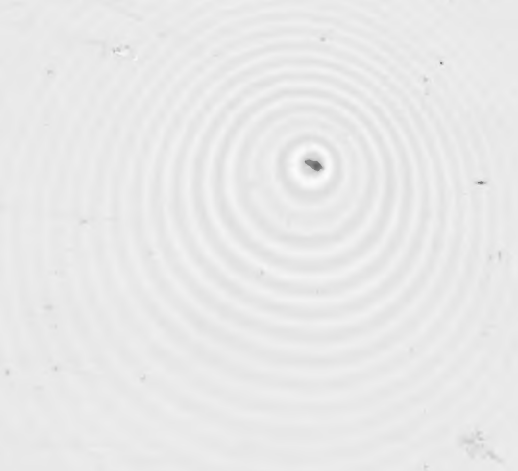
APPENDIX 3**ADDITIONAL ION INTERACTION PARAMETERS FOR THE PITZER EQUATIONS**

Table A.16: Additional ion interaction parameters: $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and C_{ca}^c at 25°C.

reference	cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^c
82	H ⁺	Cl ⁻	0.1775	0.2945	0.0	0.00080
	H ⁺	Br ⁻	0.1960	0.3564	0.0	0.00827
	H ⁺	I ⁻	0.2362	0.3920	0.0	0.00110
	Li ⁺	Cl ⁻	0.1494	0.3074	0.0	0.00359
	Li ⁺	SO ₄ ²⁻	0.136275	1.2705	0.0	-0.0039933
	Li ⁺	OH ⁻	0.0150	0.1400	0.0	0.0
	Li ⁺	Br ⁻	0.1748	0.2547	0.0	0.00530
	Li ⁺	I ⁻	0.2104	0.3730	0.0	0.0
	Na ⁺	Cl ⁻	0.0765	0.2664	0.0	0.00127
	Na ⁺	SO ₄ ²⁻	0.019575	1.1130	0.0	0.005701
	Na ⁺	CO ₃ ²⁻	0.18975	0.8460	0.0	0.0480319
	Na ⁺	OH ⁻	0.0864	0.2530	0.0	0.0044
	Na ⁺	Br ⁻	0.0973	0.2791	0.0	0.00116
	Na ⁺	I ⁻	0.1195	0.3439	0.0	0.0018
	Na ⁺	F ⁻	0.0215	0.2107	0.0	0.0
	K ⁺	Cl ⁻	0.04835	0.2122	0.0	-0.00084
	K ⁺	SO ₄ ²⁻	0.04995	0.77925	0.0	0.0
	K ⁺	OH ⁻	0.1298	0.320	0.0	0.0041
	K ⁺	Br ⁻	0.0569	0.2212	0.0	-0.00180
	K ⁺	I ⁻	0.0746	0.2517	0.0	-0.00414
	K ⁺	F ⁻	0.08089	0.2021	0.0	0.00093
	Rb ⁺	Cl ⁻	0.0441	0.1483	0.0	-0.00101
	Rb ⁺	Br ⁻	0.0396	0.1530	0.0	-0.00144
	Rb ⁺	I ⁻	0.0397	0.1330	0.0	-0.00108
	Rb ⁺	F ⁻	0.1141	0.2842	0.0	-0.0105
	Rb ⁺	SO ₄ ²⁻	0.0579	1.11075	0.0	-0.000101
	Cs ⁺	Cl ⁻	0.0300	0.0558	0.0	0.00038
	Cs ⁺	Br ⁻	0.0279	0.0139	0.0	0.00004
	Cs ⁺	I ⁻	0.0244	0.0262	0.0	-0.00365
	Cs ⁺	OH ⁻	0.150	0.30	0.0	0.0
	Cs ⁺	F ⁻	0.1306	0.2570	0.0	-0.0043
	Cs ⁺	SO ₄ ²⁻	0.0888	1.11075	0.0	-0.005998
	Ca ²⁺	Cl ⁻	0.3159	1.6140	0.0	-0.0003394
	Ca ²⁺	I ⁻	0.437925	1.80675	0.0	-0.0008379
	Ca ²⁺	Br ⁻	0.3816	1.61325	0.0	-0.0025721
	Mg ²⁺	Cl ⁻	0.35235	1.6815	0.0	0.0051919
	Mg ²⁺	Br ⁻	0.432675	1.75275	0.0	0.0031236
	Mg ²⁺	I ⁻	0.4902	1.804125	0.0	0.0079337
	Sr ²⁺	Cl ⁻	0.28575	1.66725	0.0	-0.0013046
	Sr ²⁺	Br ⁻	0.331125	1.7115	0.0	0.001225
	Sr ²⁺	I ⁻	0.40125	1.8600	0.0	0.0026569
	Ba ²⁺	Cl ⁻	0.2628	1.49625	0.0	-0.0193782
	Ba ²⁺	OH ⁻	0.17175	1.2000	0.0	0.0
	Ba ²⁺	Br ⁻	0.31455	1.56975	0.0	-0.0159576

Table A.16: continued.

reference	cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^∞
82 cont.	Ba ²⁺	I ⁻	0.421875	1.68675	0.0	-0.0174266
	Mn ²⁺	Cl ⁻	0.327225	1.55025	0.0	-0.0204972
	Fe ²⁺	Cl ⁻	0.335925	1.53225	0.0	-0.0086072
	Co ²⁺	Cl ⁻	0.364275	1.47525	0.0	-0.0152151
	Co ²⁺	Br ⁻	0.426975	1.65975	0.0	-0.0006735
	Co ²⁺	I ⁻	0.52125	1.6725	0.0	-0.0046669
	Ni ²⁺	Cl ⁻	0.347925	1.58100	0.0	-0.0037229
	Zn ²⁺	Cl ⁻	0.260175	1.6425	0.0	-0.0879817
	Zn ²⁺	Br ⁻	0.465975	1.63425	0.0	-0.1079221
	Zn ²⁺	I ⁻	0.4821	1.9455	0.0	-0.0142658
	Cu ²⁺	Cl ⁻	0.308025	1.37625	0.0	-0.0404323
	Al ³⁺	Cl ⁻	0.699333	5.844666	0.0	0.0027327
83	Mg ²⁺	SO ₄ ²⁻	0.2210	3.343	-37.23	0.0250
	Mn ²⁺	SO ₄ ²⁻	0.201	2.980	0.0	0.0182
	Ni ²⁺	SO ₄ ²⁻	0.1702	2.907	-40.06	0.0366
	Cu ²⁺	SO ₄ ²⁻	0.2358	2.485	-47.35	-0.0012
	Co ²⁺	SO ₄ ²⁻	0.20	2.70	-30.7	0.0
	Ca ²⁺	SO ₄ ²⁻	0.20	2.65	-55.7	0.0
	Be ²⁺	SO ₄ ²⁻	2.914	2.65	-40.0	0.0062
	Zn ²⁺	SO ₄ ²⁻	0.1949	2.883	-32.81	0.0290
88	H ⁺	SO ₄ ²⁻	0.2103	0.4711	0.0	0.0
	H ⁺	HSO ₄ ⁻	0.0027	0.0	0.0	0.0384
90	Al ³⁺	SO ₄ ²⁻	1.219	14.901	-2700.0	-0.04287
15	Co ²⁺	Cl ⁻	0.3582	1.44975	0.0	-0.012537
16	Cu ²⁺	SO ₄ ²⁻	0.2340	2.527	-48.33	0.0044
	Cu ²⁺	Cl ⁻	0.2966	1.391	0.0	-0.03602
85	Na ⁺	HCO ₃ ⁻	0.0277	-0.0411	0.0	0.0
	K ⁺	HCO ₃ ⁻	-0.0005	-0.0130	0.0	0.0
70	Na ⁺	CO ₃ ²⁻	0.0362	1.510	0.0	0.0052
	Na ⁺	HCO ₃ ⁻	0.028	0.044	0.0	0.0
71	Ca ²⁺	Cl ⁻	0.30534	1.7083	0.0	0.002153
112	K ⁺	HCO ₃ ⁻	-0.022	0.09	0.0	0.0
111	K ⁺	CO ₃ ²⁻	0.1288	1.433	0.0	0.00050
	K ⁺	HCO ₃ ⁻	-0.107	0.0478	0.0	0.0

Table A.16: continued.

reference	cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^∞
84	Mg ²⁺	HCO ₃ ²⁻	0.033	0.85	0.0	0.0
	Ca ²⁺	HCO ₃ ²⁻	0.280	0.3000	0.0	0.0
61	H ⁺	Cl ⁻	0.17527	0.30197	0.0	0.0014670
	K ⁺	Cl ⁻	0.04835	0.21220	0.0	-0.00084
62	Na ⁺	Cl ⁻	0.07669	0.26461	0.0	0.0012193
	Sr ²⁺	Cl ⁻	0.28994	1.5795	0.0	-0.003755
101	Na ⁺	CO ₃ ²⁻	0.040822	1.46790	0.0	0.0042374
125	Na ⁺	Cl ⁻	0.07669	0.026461	0.0	0.0012193
3	Cs ⁺	Cl ⁻	0.031310	0.065925	0.0	0.00030705
45	Ca ²⁺	Br ⁻	0.3648	1.7269	0.0	-0.004572
	H ⁺	Br ⁻	0.1905	0.3975	0.0	0.009687
46	Ba ²⁺	Br ⁻	0.3143	1.5853	0.0	-0.01579
58	Sr ²⁺	Br ⁻	0.3303	1.714	0.0	0.001749
105	Mg ²⁺	HCO ₃ ²⁻	0.490	1.900	0.0	0.0
	Ca ²⁺	HCO ₃ ²⁻	0.440	1.700	0.0	0.0
	Na ⁺	HSO ₃ ⁻	0.0249	0.2455	0.0	0.0004
	K ⁺	HSO ₃ ⁻	-0.096	0.2481	0.0	0.0
	Mg ²⁺	HSO ₃ ⁻	0.490	1.804	0.0	0.0
	Ca ²⁺	HSO ₃ ⁻	0.438	1.76	0.0	0.0
	Na ⁺	SO ₃ ²⁻	0.021	1.00	0.0	0.0
	K ⁺	SO ₃ ²⁻	0.065	1.00	0.0	0.0
	Mg ²⁺	SO ₃ ²⁻	0.200	3.00	-41.0	0.0
	Ca ²⁺	SO ₃ ²⁻	0.180	2.38	-61.3	0.0
	K ⁺	CO ₃ ²⁻	0.075	0.66	0.0	0.0
	Mg ²⁺	CO ₃ ²⁻	0.180	2.70	-46.0	0.0
	Ca ²⁺	CO ₃ ²⁻	0.160	2.10	-69.0	0.0
	Na ⁺	S ₂ O ₃ ²⁻	0.07	0.9	0.0	0.0004
	K ⁺	S ₂ O ₃ ²⁻	0.10	1.1	0.0	0.0004
	Mg ²⁺	S ₂ O ₃ ²⁻	0.24	3.7	-34.0	0.0004
	Ca ²⁺	S ₂ O ₃ ²⁻	0.22	3.0	-50.0	0.0004
93	Na ⁺	SO ₄ ²⁻	0.01869	1.099425	0.0	0.0055488
	Mg ²⁺	SO ₄ ²⁻	0.21499	3.3646	-32.743	0.02797
94	Mg ²⁺	Cl ⁻	0.35093	1.65075	0.0	0.006507

Table A.16: continued.

reference	cation	anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^2
95	Sr^{2+}	Cl^-	0.28344	1.625625	0.0	-0.0008909
	Cs^+	Cl^-	0.03917	-0.002984	0.0	-0.001183
91	Mn^{2+}	Cl^-	0.3322275	1.514625	0.0	-0.0226875
	Mn^{2+}	SO_4^{2-}	0.21300	2.9380	-41.906	0.01551
92	Ni^{2+}	Cl^-	0.33499	1.5300	0.0	-0.0047099
1	Ca^{2+}	Cl^-	0.5292	-3.9317	0.0	-0.02245
123	Ca^{2+}	Br^-	0.3562	1.872	0.0	0.005291
117	Na^+	CO_3^{2-}	-0.04096	0.5062	0.0	0.005250
66	Mg^{2+}	CO_3^{2-}	2.833	-15.069	-204.90	-0.970
	Mg^{2+}	HCO_3^-	0.0193	0.584	0.0	0.0
56	K^+	SO_4^{2-}	0.04432	0.7365	0.0	0.00181
	K	Cl	0.04626	0.21844	0.0	-0.000398
118	K^+	Cl^-	0.04626	0.21844	0.0	-0.000398
98	Al^{3+}	SO_4^{2-}	0.854	18.53	-500.0	-0.0911
99	Sr^{2+}	SO_4^{2-}	0.2000	3.1973	-78.0	0.0
100	H^+	SO_4^{2-}	0.0217	0.0	0.0	0.0411
	H^+	HSO_4^-	0.2106	0.5320	0.0	0.0
	Fe^{2+}	SO_4^{2-}	0.2568	3.063	-42.0	0.0209
	Fe^{2+}	HSO_4^-	0.4273	3.480	0.0	0.0
19	Cs^+	SO_4^{2-}	0.0714	1.2010	0.0	0.00291

Table A.17: Additional ion interaction parameters: ${}^s\theta_{cc}$, θ_{cc} , ${}^s\psi_{cca}$, ψ_{cca} and ${}^s\theta_{aa}$, θ_{aa} , ${}^s\psi_{aac}$ and ψ_{aac} at 25°C.

reference	ion	ion	ion	${}^s\theta$	${}^s\psi$	θ	ψ
81	H ⁺	Li ⁺	Cl ⁻	---	---	0.015	0.000
	H ⁺	Li ⁺	Br ⁻	---	---	0.015	0.000
	H ⁺	Na ⁺	Cl ⁻	---	---	0.036	-0.004
	H ⁺	Na ⁺	Br ⁻	---	---	0.036	-0.012
	H ⁺	K ⁺	Cl ⁻	---	---	0.005	-0.007
	H ⁺	K ⁺	Br ⁻	---	---	0.005	-0.021
	H ⁺	Cs ⁺	Cl ⁻	---	---	-0.044	-0.019
	Li ⁺	Na ⁺	Cl ⁻	---	---	0.012	-0.003
	Li ⁺	K ⁺	Cl ⁻	---	---	-0.022	-0.010
	Li ⁺	Cs ⁺	Cl ⁻	---	---	-0.095	-0.094
	Na ⁺	K ⁺	Cl ⁻	---	---	-0.012	-0.0018
	Na ⁺	K ⁺	Br ⁻	---	---	-0.012	-0.0022
	Na ⁺	K ⁺	SO ₄ ²⁻	---	---	-0.012	-0.010
	Na ⁺	Cs ⁺	Cl ⁻	---	---	-0.033	-0.003
	K ⁺	Cs ⁺	Cl ⁻	---	---	0.000	-0.0013
	H ⁺	Sr ²⁺	Cl ⁻	---	---	-0.020	0.018
	H ⁺	Ba ²⁺	Cl ⁻	---	---	-0.036	0.024
	H ⁺	Mn ²⁺	Cl ⁻	---	---	0.000	0.000
	Li ⁺	Ba ²⁺	Cl ⁻	---	---	-0.070	0.019
	Na ⁺	Mg ²⁺	Cl ⁻	---	---	0.000	0.000
	Na ⁺	Mg ²⁺	SO ₄ ²⁻	---	---	0.000	0.000
	Na ⁺	Ca ²⁺	Cl ⁻	---	---	0.000	0.000
	Na ⁺	Ba ²⁺	Cl ⁻	---	---	-0.003	0.000
	Na ⁺	Mn ²⁺	Cl ⁻	---	---	0.000	-0.003
	Na ⁺	Zn ²⁺	Br ⁻	---	---	0.000	0.000
	K ⁺	Ca ²⁺	Cl ⁻	---	---	-0.040	-0.015
	K ⁺	Ba ²⁺	Cl ⁻	---	---	-0.072	0.000
	Cs ⁺	Ba ²⁺	Cl ⁻	---	---	-0.150	0.000
	Mg ²⁺	Ca ²⁺	Cl ⁻	---	---	0.010	0.000
	Na ⁺	Cl ⁻	Br ⁻	---	---	0.000	0.000
	K ⁺	Cl ⁻	Br ⁻	---	---	0.000	0.000
	Na ⁺	Cl ⁻	OH ⁻	---	---	-0.050	-0.006
	K ⁺	Cl ⁻	OH ⁻	---	---	-0.050	-0.008
	Na ⁺	Br ⁻	OH ⁻	---	---	-0.065	-0.018
	K ⁺	Br ⁻	OH ⁻	---	---	-0.065	-0.014
	Na ⁺	Cl ⁻	SO ₄ ²⁻	---	---	-0.035	0.007
	K ⁺	Cl ⁻	SO ₄ ²⁻	---	---	-0.035	0.000
	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	---	---	-0.035	0.000
77	H ⁺	Sr ²⁺	Cl ⁻	0.065	0.003	---	---
	H ⁺	Ba ²⁺	Cl ⁻	0.072	0.000	---	---
	H ⁺	Mn ²⁺	Cl ⁻	0.075	-0.007	---	---
	Li ⁺	Ba ²⁺	Cl ⁻	0.000	0.009	---	---

Table A.17: continued.

reference	ion	ion	ion	θ	ψ	θ	ψ
77 cont.	Na ⁺	Mg ²⁺	Cl ⁻	0.070	-0.010	---	---
	Na ⁺	Mg ²⁺	SO ₄ ²⁻	0.070	-0.023	---	---
	Na ⁺	Ca ²⁺	Cl ⁻	0.070	-0.007	---	---
	Na ⁺	Ba ²⁺	Cl ⁻	0.067	-0.012	---	---
	Na ⁺	Mn ²⁺	Cl ⁻	0.082	-0.0174	---	---
	K ⁺	Ca ²⁺	Cl ⁻	0.032	-0.025	---	---
	K ⁺	Ba ²⁺	Cl ⁻	0.010	-0.017	---	---
	Cs ⁺	Ba ²⁺	Cl ⁻	-0.070	-0.015	---	---
	Na ⁺	Cl ⁻	SO ₄ ²⁻	0.020	0.0014	---	---
	K ⁺	Cl ⁻	SO ₄ ²⁻	0.020	0.000	---	---
	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	0.020	-0.014	---	---
	H ⁺	Al ³⁺	Cl ⁻	0.185	0.013	---	---
88	H ⁺	SO ₄ ²⁻	HSO ₄ ⁻	---	---	0.000	0.000
85	Na ⁺	Cl ⁻	HCO ₃ ⁻	---	---	0.030	---
70	Na ⁺	Cl ⁻	CO ₃ ²⁻	-0.053	---	-0.092	---
	Na ⁺	Cl ⁻	HCO ₃ ⁻	---	---	0.0359	-0.0143
84	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	---	---	0.0359	0.0
	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	---	---	0.0359	0.0
15	Na ⁺	Co ²⁺	Cl ⁻	---	---	-0.016	-0.001
	Ca ²⁺	Co ²⁺	Cl ⁻	---	---	-0.055	0.013
16	Na ⁺	Cu ²⁺	Cl ⁻	0.077	-0.026	0.000	-0.014
	Na ⁺	Cu ²⁺	SO ₄ ²⁻	0.077	-0.049	0.000	-0.011
	Na ⁺	Cl ⁻	SO ₄ ²⁻	0.030	0.000	-0.020	0.004
	Cu ²⁺	Cl ⁻	SO ₄ ²⁻	0.030	0.031	-0.020	0.043
	K ⁺	Cl ⁻	SO ₄ ²⁻	0.030	-0.005	-0.020	-0.007
	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	0.030	-0.020	-0.020	-0.007
110	H ⁺	Mn ²⁺	Cl ⁻	0.0834	-0.0090	-0.0010	0.0014
				0.0770	-0.00005	---	---
106	H ⁺	Mg ²⁺	Cl ⁻	0.0620	0.0010	-0.024	0.0122
	H ⁺	Ni ²⁺	Cl ⁻	0.0782	0.0035	0.0058	0.0090
107	H ⁺	Ca ²⁺	Cl ⁻	0.0612	0.0008	-0.0333	0.0160
111	K ⁺	Cl ⁻	CO ₃ ²⁻	-0.053	0.024	-0.092	0.0073
	K ⁺	Cl ⁻	HCO ₃ ⁻	---	---	0.0359	-0.0037
	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	0.089	-0.036	-0.063	0.013

Table A.17: continued.

reference	ion	ion	ion	θ	ψ	θ	ψ
114	H ⁺	Ca ²⁺	Br ⁻	0.0832	-0.0083	-0.0394	0.0298
40	H ⁺	Ca ²⁺	Cl ⁻	---	---	-0.0628	0.0467
41	H ⁺	Mg ²⁺	Cl ⁻	---	---	-0.0459	0.0396
42	H ⁺	Ba ²⁺	Cl ⁻	---	---	-0.0616	0.0424
43	H ⁺	Ni ²⁺	Cl ⁻	0.0818	0.0051	-0.0559	0.0475
44	H ⁺	Co ²⁺	Cl ⁻	0.0787	0.0064	-0.0597	0.0493
	H ⁺	Sr ²⁺	Cl ⁻	0.0720	0.0007	-0.0311	0.0178
	H ⁺	Mn ²⁺	Cl ⁻	0.0694	-0.0006	-0.0666	0.0386
	H ⁺	Mg ²⁺	Cl ⁻	0.0897	-0.0014	---	---
	H ⁺	Ca ²⁺	Cl ⁻	0.0739	0.0030	---	---
	H ⁺	Ba ²⁺	Cl ⁻	0.0763	-0.0001	---	---
45	H ⁺	Ca ²⁺	Br ⁻	0.0600	0.0163	-0.1038	0.0918
12	H ⁺	K ⁺	Cl ⁻	---	---	0.0068	-0.0106
13	H ⁺	Na ⁺	Cl ⁻	---	---	0.0279	0.0105
	H ⁺	K ⁺	Cl ⁻	---	---	0.0074	-0.0105
46	H ⁺	Ba ²⁺	Br ⁻	0.0719	0.0057	-0.0921	0.0812
61	H ⁺	K ⁺	Cl ⁻	0.00084	-0.0079	0.0031	-0.0085
62	Na ⁺	Sr ²⁺	Cl ⁻	-0.0076	-0.0052	-0.0084	0.0036
125	Na ⁺	Cl ⁻	CO ₃ ²⁻	---	---	-0.1605	0.05030
126	Mg ²⁺	H ⁺	Cl ⁻	-0.4357	0.3843	-0.1401	0.5337
3	Cs ⁺	K ⁺	Cl ⁻	---	---	-0.0065	0.0013
31	Na ⁺	K ⁺	Cl ⁻	---	---	-0.0154	-0.00078
32	Na ⁺	Ca ²⁺	Cl ⁻	---	---	-0.0078	0.0029
117	Na ⁺	CO ₃ ²⁻	HCO ₃ ⁻	---	---	0.020	0.010
122	Na ⁺	Cl ⁻	CO ₃ ²⁻	-0.053	0.016	-0.092	0.006
95	Na ⁺	Cs ⁺	Cl ⁻	---	---	-0.03886	-0.00135

Table A.17: continued.

reference	ion	ion	ion	θ	ψ	θ	ψ
96	Na ⁺	Sr ²⁺	Cl ⁻	---	---	0.00940	-0.00323
97	Na ⁺	Mg ²⁺	Cl ⁻	---	---	0.016271	-0.004585
57	Li ⁺	Ni ²⁺	Cl ⁻	---	---	-0.059	0.047
56	K ⁺	Mg ²⁺	SO ₄ ²⁻	-0.0048	0.0	-0.031	0.0
	K ⁺	Mg ²⁺	Cl ⁻	-0.0113	0.0	0.0371	0.0
19	Li ⁺	Cs ⁺	SO ₄ ²⁻	---	---	-0.1242	0.0088
	Na ⁺	Cs ⁺	SO ₄ ²⁻	---	---	-0.0153	-0.0035
	K ⁺	Cs ⁺	SO ₄ ²⁻	---	---	-0.0049	-0.0016
98	Al ³⁺	Mg ²⁺	SO ₄ ²⁻	---	---	0.0	0.030
	Al ³⁺	Ca ²⁺	SO ₄ ²⁻	---	---	0.0	0.030
	Al ³⁺	Fe ²⁺	SO ₄ ²⁻	---	---	0.0	0.0
99	Na ⁺	Sr ²⁺	Cl ⁻	0.051	-0.0021	---	---
	Na ⁺	Sr ²⁺	SO ₄ ²⁻	0.051	---	---	---
100	H ⁺	Fe ²⁺	SO ₄ ²⁻	3.50	0.0	---	---
	H ⁺	Fe ²⁺	HSO ₄	3.50	0.0143	---	---
	Fe ²⁺	SO ₄ ²⁻	HSO ₄	0.0	0.0143	---	---

Table A.18: Values of $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and C_{ca}^2 at temperatures other than 25°C.

reference	cation	anion	temp.(°C)	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^2
30	K ⁺	Cl ⁻	108.9	0.07039	0.34346	0.0	-0.00323
			140.6	0.07096	0.40127	0.0	-0.00340
			172.3	0.07123	0.43505	0.0	-0.00345
			200.9	0.07060	0.46056	0.0	-0.00344
	Ca ⁺²	Cl ⁻	108.9	0.30353	2.2780	0.0	-0.00868
			140.6	0.29054	2.6045	0.0	-0.01043
			172.3	0.28151	2.8545	0.0	-0.01269
			200.9	0.27035	3.3215	0.0	-0.01367
	Mg ⁺²	Cl ⁻	108.9	0.30719	2.2274	0.0	-0.00097
			140.6	0.29373	2.5026	0.0	-0.00235
			172.3	0.27583	2.9112	0.0	-0.00217
			200.9	0.26935	3.2518	0.0	-0.00395
33	Ni ⁺²	Cl ⁻	25.0 ¹	0.3479	1.581	0.0	-0.00372
			109.8	0.2955	1.947	0.0	-0.0153
			140.2	0.2737	1.813	0.0	-0.0171
	Co ⁺²	Cl ⁻	25.0 ¹	0.3643	1.475	0.0	-0.0152
			109.8	0.2908	1.851	0.0	-0.0234
			140.2	0.2182	2.325	0.0	-0.0161
34	Sr ⁺²	Cl ⁻	25.0 ¹	0.28575	1.66725	0.0	-0.000689
			109.8	0.2890	2.120	0.0	-0.01193
			140.2	0.2835	2.264	0.0	-0.01528
			170.8	0.2763	2.410	0.0	-0.01720
			200.5	0.2619	2.923	0.0	-0.01701
	Ba ⁺²	Cl ⁻	25.0 ¹	0.26280	1.49825	0.0	-0.0102778
			109.8	0.2706	1.937	0.0	-0.02631
			140.2	0.2593	2.148	0.0	-0.02590
			170.8	0.2458	2.454	0.0	-0.02487
			200.5	0.2314	2.832	0.0	-0.02299
35	Li ⁺	Cl ⁻	25.0 ¹	0.1494	0.3074	0.0	-0.000359
			109.8	0.1347	0.3766	0.0	0.00055
			140.2	0.1313	0.3756	0.0	-0.00069
			170.8	0.1262	0.4053	0.0	-0.00119
			200.5	0.1190	0.4439	0.0	-0.00142

Table A.18: continued.

reference	cation	anion	temp.(°C)	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C°
35 cont.	Cs ⁺	Cl ⁻	25.0 ¹	0.0300	0.0558	0.0	0.00038
			109.8	0.0581	0.1800	0.0	-0.00228
			140.2	0.0586	0.2542	0.0	-0.00223
			170.8	0.0595	0.2977	0.0	-0.00224
			200.5	0.0603	0.3297	0.0	-0.00230
36	Mg ²⁺	SO ₄ ²⁻	25.0 ²	0.2210	3.343	-37.23	0.0250
			110.0	0.2370	4.742	0.0	0.00318
	Ni ²⁺	SO ₄ ²⁻	25.0 ²	0.1702	2.907	-40.06	0.0366
			110.0	0.1888	4.784	0.0	0.01461
39	Li ⁺	SO ₄ ²⁻	25.0	0.1339	1.282	0.0	-0.00333
			110.0	0.1333	1.575	0.0	-0.01200
			140.1	0.1254	1.722	0.0	-0.01245
			170.0	0.1200	2.150	0.0	-0.01215
			200.0	0.1258	2.268	0.0	-0.01526
			225.0	0.1212	2.952	0.0	-0.01329
	Na ⁺	SO ₄ ²⁻	25.0	0.0148	1.218	0.0	0.00634
			110.0	0.0949	1.718	0.0	-0.00971
			140.1	0.0990	1.949	0.0	-0.01077
			170.0	0.1079	2.301	0.0	-0.01299
			200.0	0.1076	2.694	0.0	-0.01184
			225.0	0.1162	3.104	0.0	-0.01266
	K ⁺	SO ₄ ²⁻	25.0	0.0927	0.603	0.0	-0.03661
			110.0	0.1310	1.225	0.0	-0.02424
			140.1	0.1290	1.521	0.0	-0.01842
			170.0	0.1348	2.004	0.0	-0.01708
			200.0	0.1532	2.235	0.0	-0.02128
			225.0	0.1534	2.829	0.0	-0.01798
	Cs ⁺	SO ₄ ²⁻	25.0	0.0882	1.105	0.0	-0.00795
			110.0	0.1309	1.574	0.0	-0.00612
			140.1	0.1361	1.968	0.0	-0.00688
			170.0	0.1422	2.438	0.0	-0.00754
			200.0	0.1488	3.119	0.0	-0.00814
			225.0	0.1580	3.992	0.0	-0.00877
7	Na ⁺	SO ₄ ²⁻	50.0	0.0477	1.37	0.0	0.00237
			75.0	0.0894	1.29	0.0	-0.00613
			100.0	0.1230	1.25	0.0	-0.01250
			125.0	0.1390	1.17	0.0	-0.01400
			150.0	0.1040	1.10	0.0	-0.00551

Table A.18: continued.

reference	cation	anion	temp.(°C)	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C°
8	Na ⁺	SO ₄ ²⁻	150.0	0.0708	1.9066	0.0	0.0098
			175.0	0.1243	0.1732	0.0	-0.0113
			200.0	0.1149	-0.4343	0.0	-0.0115
			225.0	0.1029	0.0840	0.0	-0.0065
			250.0	0.1413	0.17282	0.0	-0.0077
11	Na ⁺	OH ⁻	150.0	0.0388	0.6522	0.0	0.0039
			175.0	0.0100	0.8230	0.0	0.0092
			200.0	0.0029	0.9209	0.0	0.0113
			225.0	0.0044	0.9459	0.0	0.0126
			250.0	0.0105	0.8982	0.0	0.0144

1: 25°C values from reference 82

2: 25°C value from reference 83.

Table A.19: Temperature derivatives of $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and C_{ca}^∞ .

reference	cation	anion	max. temp. (°C)	$\frac{\partial\beta^{(0)}}{\partial T}$	$\frac{\partial\beta^{(1)}}{\partial T}$	$\frac{\partial\beta^{(2)}}{\partial T}$	$\frac{\partial C^\infty}{\partial T}$
119	H ⁺	Cl ⁻	50.0	-3.081x10 ⁻⁴	1.419x10 ⁻⁴	0.0	6.213x10 ⁻⁵
	H ⁺	Br ⁻	50.0	-2.049x10 ⁻⁴	4.467x10 ⁻⁴	0.0	-5.685x10 ⁻⁵
	H ⁺	I ⁻	50.0	-0.230x10 ⁻⁴	8.860x10 ⁻⁴	0.0	-7.320x10 ⁻⁵
	Li ⁺	Cl ⁻	50.0	-1.685x10 ⁻⁴	5.366x10 ⁻⁴	0.0	-4.520x10 ⁻⁵
	Li ⁺	Br ⁻	50.0	-1.819x10 ⁻³	6.636x10 ⁻³	0.0	-2.813x10 ⁻⁵
	Na ⁺	F ⁻	50.0	5.361x10 ⁻⁴	8.70x10 ⁻⁴	0.0	0.0
	Na ⁺	Cl ⁻	50.0	7.159x10 ⁻⁴	7.005x10 ⁻⁴	0.0	-1.054x10 ⁻⁴
	Na ⁺	Br ⁻	50.0	7.692x10 ⁻⁴	1.079x10 ⁻³	0.0	9.30x10 ⁻⁵
	Na ⁺	I ⁻	50.0	8.355x10 ⁻⁴	8.28x10 ⁻⁴	0.0	-8.350x10 ⁻⁵
	Na ⁺	OH ⁻	50.0	7.00x10 ⁻⁴	1.34x10 ⁻⁴	0.0	-1.894x10 ⁻⁴
	K ⁺	F ⁻	50.0	2.14x10 ⁻⁴	5.44x10 ⁻⁴	0.0	-5.95x10 ⁻⁵
	K ⁺	Cl ⁻	50.0	5.794x10 ⁻⁴	1.071x10 ⁻³	0.0	-5.095x10 ⁻⁵
	K ⁺	Br ⁻	50.0	7.39x10 ⁻⁴	1.740x10 ⁻³	0.0	-7.004x10 ⁻⁵
	K ⁺	I ⁻	50.0	9.914x10 ⁻⁴	1.186x10 ⁻³	0.0	-9.44x10 ⁻⁵
	Cs ⁺	Cl ⁻	50.0	8.28x10 ⁻⁴	1.50x10 ⁻³	0.0	-1.225x10 ⁻⁴
	Cs ⁺	I ⁻	50.0	9.75x10 ⁻⁴	3.477x10 ⁻³	0.0	0.0
	Cs ⁺	F ⁻	50.0	0.95x10 ⁻⁴	5.97x10 ⁻⁴	0.0	0.0
	Cs ⁺	Br ⁻	50.0	7.80x10 ⁻⁴	2.844x10 ⁻³	0.0	0.0
	Rb ⁺	Cl ⁻	50.0	5.52x10 ⁻⁴	1.506x10 ⁻³	0.0	0.0
	Rb ⁺	I ⁻	50.0	8.578x10 ⁻⁴	2.383x10 ⁻³	0.0	0.0
	Rb ⁺	F ⁻	50.0	-0.76x10 ⁻⁴	1.47x10 ⁻³	0.0	0.0
	Rb ⁺	Br ⁻	50.0	6.780x10 ⁻⁴	2.035x10 ⁻³	0.0	0.0
	Mg ²⁺	Cl ⁻	50.0	-1.9425x10 ⁻⁴	2.775x10 ⁻⁴	0.0	-1.6493x10 ⁻⁵
	Mg ²⁺	Br ⁻	50.0	-0.0523x10 ⁻³	3.8625x10 ⁻³	0.0	0.0
	Ca ²⁺	Cl ⁻	50.0	-0.1725x10 ⁻⁴	3.9000x10 ⁻⁴	0.0	0.0
	Ca ²⁺	Br ⁻	50.0	-0.52275x10 ⁻³	6.0375x10 ⁻³	0.0	0.0
	Sr ²⁺	Cl ⁻	50.0	0.7170x10 ⁻³	2.8425x10 ⁻³	0.0	0.0
	Sr ²⁺	Br ⁻	50.0	-0.3278x10 ⁻³	6.5325x10 ⁻³	0.0	0.0
	Ba ²⁺	Cl ⁻	50.0	0.6405x10 ⁻³	3.2325x10 ⁻³	0.0	-1.53796x10 ⁻⁴
	Ba ²⁺	Br ⁻	50.0	-0.3383x10 ⁻³	6.785x10 ⁻³	0.0	0.0
	Cu ²⁺	Cl ⁻	50.0	-2.715x10 ⁻³	8.475x10 ⁻³	0.0	0.0
	Li ⁺	SO ₄ ²⁻	50.0	0.5055x10 ⁻³	1.41x10 ⁻³	0.0	-2.3335x10 ⁻⁴
	Na ⁺	SO ₄ ²⁻	50.0	2.367x10 ⁻³	5.6325x10 ⁻³	0.0	-4.8790x10 ⁻⁴
	K ⁺	SO ₄ ²⁻	50.0	1.440x10 ⁻³	6.6975x10 ⁻³	0.0	0.0
	Ca ²⁺	SO ₄ ²⁻	50.0	0.0	5.46x10 ⁻²	-0.516	0.0
	Cu ²⁺	SO ₄ ²⁻	50.0	-4.4x10 ⁻³	2.38x10 ⁻²	-0.473	4.80x10 ⁻³
	Zn ²⁺	SO ₄ ²⁻	50.0	-3.66x10 ⁻³	2.33x10 ⁻²	0.333	3.97x10 ⁻³
	Cs ⁺	SO ₄ ²⁻	50.0	-8.925x10 ⁻⁴	1.4483x10 ⁻²	0.0	0.0
	Rb ⁺	SO ₄ ²⁻	50.0	9.375x10 ⁻⁴	8.64x10 ⁻³	0.0	0.0
	Mg ²⁺	SO ₄ ²⁻	50.0	-6.90x10 ⁻⁴	1.53x10 ⁻²	0.253	5.25x10 ⁻⁴

Table A.19: continued.

reference	cation	anion	max. temp. (°C)	$\frac{\partial \beta^{(0)}}{\partial T}$	$\frac{\partial \beta^{(1)}}{\partial T}$	$\frac{\partial \beta^{(2)}}{\partial T}$	$\frac{\partial C^{\infty}}{\partial T}$
103	Na ⁺	SO ₄ ²⁻	50.0	2.349x10 ⁻³	5.958x10 ⁻³	0.0	-4.79x10 ⁻⁵
112	K ⁺	CO ₃ ²⁻	50.0	1.788x10 ⁻³	2.051x10 ⁻³	0.0	0.0
	K ⁺	HCO ₃ ⁻	50.0	0.996x10 ⁻³	1.104x10 ⁻³	0.0	0.0
111	K ⁺	CO ₃ ²⁻	50.0	1.1x10 ⁻³	4.36x10 ⁻³	0.0	0.0
116	Na ⁺	I ⁻	---	9.163x10 ⁻⁴	9.964x10 ⁻⁴	0.0	-5.58x10 ⁻⁵
	H ⁺	Cl ⁻	---	-3.081x10 ⁻⁴	1.419x10 ⁻⁴	0.0	3.106x10 ⁻⁵
	Cs ⁺	I ⁻	---	9.75x10 ⁻⁴	3.477x10 ⁻³	0.0	0.0
	Cs ⁺	F ⁻	---	0.95x10 ⁻⁴	5.97x10 ⁻⁴	0.0	0.0
	Cs ⁺	Cl ⁻	---	7.030x10 ⁻⁴	2.107x10 ⁻³	0.0	-4.06x10 ⁻⁵
72	Li ⁺	Cl ⁻	100.0	-1.746x10 ⁻⁴	8.008x10 ⁻⁴	0.0	2.184x10 ⁻⁵
	Li ⁺	Br ⁻	100.0	-1.585x10 ⁻⁴	8.507x10 ⁻⁴	0.0	-1.571x10 ⁻⁵
	Na ⁺	F ⁻	100.0	5.596x10 ⁻⁴	4.588x10 ⁻⁴	0.0	0.0
	Na ⁺	Br ⁻	100.0	8.126x10 ⁻⁴	9.843x10 ⁻⁴	0.0	-5.252x10 ⁻⁵
	K ⁺	F ⁻	100.0	2.209x10 ⁻⁴	6.275x10 ⁻⁴	0.0	-3.199x10 ⁻⁵
	K ⁺	Cl ⁻	100.0	6.789x10 ⁻⁴	9.598x10 ⁻⁴	0.0	-4.148x10 ⁻⁵
	K ⁺	Br ⁻	100.0	8.129x10 ⁻⁴	12.756x10 ⁻⁴	0.0	-4.191x10 ⁻⁵
	K ⁺	I ⁻	100.0	9.952x10 ⁻⁴	15.461x10 ⁻⁴	0.0	-4.912x10 ⁻⁵
	Li ⁺	SO ₄ ²⁻	100.0	4.454x10 ⁻⁴	24.49x10 ⁻⁴	0.0	-7.65x10 ⁻⁵
	Mg ²⁺	Br ⁻	100.0	2.872x10 ⁻⁴	33.99x10 ⁻⁴	0.0	0.0
73	Ba ²⁺	Cl ⁻	100.0	5.105x10 ⁻⁴	37.46x10 ⁻⁴	0.0	-3.13x10 ⁻⁵
	Mg ²⁺	SO ₄ ²⁻	---	2.8402x10 ⁻⁴	1.1028x10 ⁻²	0.11515	-8.7899x10 ⁻⁵
109	Sr ²⁺	Cl ⁻	50.0	-3.073x10 ⁻⁴	122.379x10 ⁻⁴	0.0	-6.688x10 ⁻⁴
114	Ca ²⁺	Br ⁻	45.0	2.744x10 ⁻³	1.669x10 ⁻³	0.0	-0.8128x10 ⁻³
75	Mg ²⁺	Cl ⁻	---	-9.8786x10 ⁻⁵	2.666x10 ⁻³	0.0	-7.624x10 ⁻⁵
	Ca ²⁺	Cl ⁻	---	1.8215x10 ⁻⁴	3.554x10 ⁻³	0.0	-4.754x10 ⁻⁵
	Sr ²⁺	Cl ⁻	---	4.3709x10 ⁻⁴	3.674x10 ⁻³	0.0	-5.070x10 ⁻⁵
99	Sr ²⁺	SO ₄ ²⁻	90.0	0.0	5.46x10 ⁻²	-9.20	0.0

Table A.19: continued.

reference	cation	anion	max. temp. (°C)	$\frac{\partial\beta^{(0)}}{\partial T}$	$\frac{\partial\beta^{(1)}}{\partial T}$	$\frac{\partial\beta^{(2)}}{\partial T}$	$\frac{\partial C^\infty}{\partial T}$
70 1,2	Na ⁺	CO ₃ ²⁻	50.0	1.79x10 ⁻³	2.05x10 ⁻³	0.0	0.0
				(-4.22x10 ⁻⁵)	(-1.68x10 ⁻⁴)	(0.0)	(0.0)
	Na ⁺	HCO ₃ ⁻	50.0	1.00x10 ⁻³	1.10x10 ⁻³	0.0	0.0
				(-2.6x10 ⁻⁵)	(-4.3x10 ⁻⁵)	(0.0)	(0.0)
	Na ⁺	OH ⁻	50.0	0.7x10 ⁻³	0.134x10 ⁻³	0.0	-1.894x10 ⁻⁴
				(-2.00x10 ⁻⁵)	(-2.1x10 ⁻⁵)	(0.0)	(0.29x10 ⁻⁵)

1: values in brackets are: $\frac{\partial^2\beta^{(0)}}{\partial T^2}$, $\frac{\partial^2\beta^{(1)}}{\partial T^2}$, $\frac{\partial^2\beta^{(2)}}{\partial T^2}$, $\frac{\partial^2 C^\infty}{\partial T^2}$

2: values of $\frac{\partial\beta^{(0)}}{\partial T}$, $\frac{\partial\beta^{(1)}}{\partial T}$, $\frac{\partial\beta^{(2)}}{\partial T}$, $\frac{\partial C^\infty}{\partial T}$ for reference 70 are from reference 120.

Table A.20: Functions for interpolating values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^* to temperatures other than 25°C.

reference	cation	anion	temp range
3	Ca ²⁺	Cl ⁻	0.0 - 100.0
14	Na ⁺	Cl ⁻	60.0 - 250.0
	K ⁺	Cl ⁻	60.0 - 250.0
	K ⁺	SO ₄ ²⁻	60.0 - 250.0
36	Mg ²⁺	SO ₄ ²⁻	25.0 - 110.0
37	Li ⁺	Cl ⁻	0.0 - 250.0
	K ⁺	Cl ⁻	0.0 - 250.0
	Cs ⁺	Cl ⁻	0.0 - 250.0
38	Na ⁺	SO ₄ ²⁻	0.0 - 225.0
	K ⁺	SO ₄ ²⁻	0.0 - 225.0
	Li ⁺	SO ₄ ²⁻	25.0 - 225.0
	Cs ⁺	SO ₄ ²⁻	25.0 - 225.0
50	Ca ²⁺	Cl ⁻	50.0 - 200.0
60	Mg ²⁺	Cl ⁻	25.0 - 300.0
68	Na ⁺	OH ⁻	0.0 - 350.0
71	Ca ²⁺	Cl ⁻	25.0 - 175.0
73	Mg ²⁺	SO ₄ ²⁻	25.0 - 200.0
75	Mg ²⁺	Cl ⁻	0.0 - 200.0
	Ca ²⁺	Cl ⁻	0.0 - 200.0
	Sr ²⁺	Cl ⁻	0.0 - 200.0
88	H ⁺	SO ₄ ²⁻	0.0 - 50.0
	H ⁺	HSO ₄ ⁻	0.0 - 50.0
	H ⁺	Cl ⁻	0.0 - 50.0
100	Fe ²⁺	SO ₄ ²⁻	10.0 - 90.0
	Fe ²⁺	HSO ₄ ⁻	10.0 - 90.0
	H ⁺	SO ₄ ²⁻	10.0 - 90.0
	H ⁺	HSO ₄ ⁻	10.0 - 90.0

Table A.20: continued.

reference	cation	anion	temp range
103	Na ⁺	SO ₄ ²⁻	25.0 - 200.0
115	H ⁺	Cl ⁻	25.0 - 350.0
116	Na ⁺	I ⁻	25.0 - 115.0
	H ⁺	Cl ⁻	25.0 - 110.0
	Cs ⁺	F ⁻	25.0 - 115.0
	Cs ⁺	I ⁻	25.0 - 115.0
	Cs ⁺	Cl ⁻	25.0 - 115.0
119	Na ⁺	Cl ⁻	0.0 - 300.0
121	K ⁺	CO ₃ ²⁻	65.0 - 95.0
124	H ⁺	Cl ⁻	10.0 - 140.0

Table A.21: Ion interaction parameters: ${}^s\theta_{cc}$, θ_{cc} , ${}^s\psi_{cca}$, ψ_{cca} , and ${}^s\theta_{aa}$, θ_{aa} , ${}^s\psi_{aac}$ and ψ_{aac} at temperatures other than 25°C

reference	ion	ion	ion	temp.(°C)	${}^s\theta$	${}^s\psi$	θ	ψ
31	Na ⁺	K ⁺	Cl ⁻	25.0	---	---	-0.0154	-0.00078
				109.6	---	---	-0.0136	0.00007
				140.3	---	---	-0.0147	0.00052
				172.1	---	---	-0.0155	0.00068
				201.0	---	---	-0.0130	0.00054
32	Na ⁺	Ca ²⁺	Cl ⁻	25.0	---	---	-0.0078	0.0029
				110.4	---	---	-0.0068	0.0001
				139.9	---	---	-0.0073	0.0004
				172.0	---	---	-0.0077	0.0004
				201.0	---	---	-0.0105	0.0004
106	H ⁺	Mg ²⁺	Cl ⁻	5.0	0.0725	0.0086	-0.012	0.0235
				15.0	0.0705	0.0063	-0.016	0.0165
				25.0	0.0620	0.0010	-0.024	0.0122
				35.0	0.0670	-0.0071	-0.028	-0.0068
				45.0	0.0856	-0.0207	-0.011	-0.0070
109	H ⁺	Sr ²⁺	Cl ⁻	5.0	0.0486	0.0099	-0.0499	0.0268
				15.0	0.0528	0.0081	-0.0500	0.0267
				25.0	0.0642	0.0033	-0.0378	0.0208
				35.0	0.0648	0.0042	-0.0425	0.0240
				45.0	0.0653	0.0012	-0.0403	0.0189
114	H ⁺	Mg ²⁺	Cl ⁻	5.0	0.0945	-0.0043	-0.0183	0.0208
				15.0	0.0857	-0.0025	-0.0325	0.0258
				25.0	0.0832	-0.0083	-0.0394	0.0298
				35.0	0.0736	0.0083	-0.0373	0.0318
				45.0	0.0615	0.0141	-0.0967	0.0577

Table A.22: Functions for interpolating values of ${}^s\theta_{cc}$, θ_{cc} , ${}^s\psi_{cca}$ and ψ_{cca} , and ${}^s\theta_{aa}$, θ_{aa} , ${}^s\psi_{aac}$ and ψ_{aac} to temperatures other than 25°C.

reference	ion	ion	ion	temp. range (°C)	
31	Na ⁺	K ⁺	Cl ⁻	? - 201.0	functions for θ ; $\psi = 0$.
32	Na ⁺	Ca ²⁺	Cl ⁻	? - 201.0	function for θ only.
109	H ⁺	Sr ²⁺	Cl ⁻	0.0 - 50.0	functions for ${}^s\theta$ and ${}^s\psi$. (derivatives presented)
114	H ⁺	Ca ²⁺	Br ⁻	0.0 - 50.0	functions for ${}^s\theta$ and ${}^s\psi$, and θ and ψ . (derivatives presented)
69	Na ⁺	K ⁺	Cl ⁻	0.0 - 150.0	function for ${}^s\psi$; ${}^s\theta$ is constant.
	Na ⁺	Mg ²⁺	Cl ⁻	0.0 - 200.0	function for ${}^s\psi$; ${}^s\theta$ is constant.
	K ⁺	Mg ²⁺	Cl ⁻	0.0 - 200.0	function for ${}^s\psi$; ${}^s\theta$ is constant.
	Cl ⁻	SO ₄ ²⁻	K ⁺	0.0 - 100.0	${}^s\psi$ and ${}^s\theta$ are constant.
	Cl ⁻	SO ₄ ²⁻	Na ⁺	0.0 - 200.0	${}^s\psi$ and ${}^s\theta$ are constant.
	Cl ⁻	SO ₄ ²⁻	Mg ²⁺	0.0 - 100.0	function for ${}^s\psi$; ${}^s\theta$ is constant.
	Cl ⁻	OH ⁻	Na ⁺	0.0 - 180.0	function for ${}^s\psi$; ${}^s\theta$ is constant.
	SO ₄ ²⁻	OH ⁻	Na ⁺	0.0 - 200.0	function for ${}^s\psi$; ${}^s\theta$ is constant.

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APPENDIX 4

**PUBLISHED REGRESSION EQUATIONS
USED TO CALCULATE $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and C^* to 200°C.**

NaCl (Silvester and Pitzer, 1977):

$$B^{(0)}(T) = B^{(0)}(T_R) + a_1[T^1 - T_R^1] + a_2[\ln T - \ln T_R] + a_3[T - T_R] + a_4[T^2 - T_R^2] \quad (25)$$

$$B^{(1)}(T) = B^{(1)}(T_R) + a_5[T - T_R] + a_6[T^2 - T_R^2] \quad (26)$$

$$C^*(T) = C^*(T_R) + a_7[T^1 - T_R^1] + a_8[\ln T - \ln T_R] + a_9[T - T_R] \quad (27)$$

KCl (Holmes and Mesmer, 1983):

$$B^{(0)}(T) = B^{(0)}(T_R) + a_1[T^1 - T_R^1] + a_2[\ln T - \ln T_R] + a_3[T - T_R] + a_4[T^2 - T_R^2] \quad (28)$$

$$B^{(1)}(T) = B^{(1)}(T_R) + a_5[T^1 - T_R^1] + a_6[\ln T - \ln T_R] + a_7 \ln [T - 260] \quad (29)$$

$$C^*(T) = C^*(T_R) + a_8[T^1 - T_R^1] + a_9[\ln T - \ln T_R] + a_{10}[T - T_R] + a_{11}[T^2 - T_R^2] \quad (30)$$

LiCl (Holmes and Mesmer, 1983):

$$B^{(0)}(T) = B^{(0)}(T_R) + a_1[T - T_R] \quad (31)$$

$$B^{(1)}(T) = B^{(1)}(T_R) + a_2[T - T_R] \quad (32)$$

$$C^*(T) = C^*(T_R) + a_3[T^1 - T_R^1] + a_4[T - T_R] \quad (33)$$

CsCl (Holmes and Mesmer, 1983):

$$B^{(0)}(T) = B^{(0)}(T_R) + a_1[T^1 - T_R^1] + a_2[\ln T - \ln T_R] + a_3[T - T_R] + a_4[T^2 - T_R^2] \quad (34)$$

$$B^{(1)}(T) = B^{(1)}(T_R) + a_5[T^1 - T_R^1] + a_6[T - T_R] \quad (35)$$

$$C^*(T) = C^*(T_R) + a_7[T^1 - T_R^1] + a_8[\ln T - \ln T_R] + a_9[T - T_R] + a_{10}[T^2 - T_R^2] \quad (36)$$

HCl (Ruaya and Seward, 1987):

$$B^{(0)}(T) = B^{(0)}(T_R) + a_1[T^1 - T_R^1] + a_2[\ln T - \ln T_R] + a_3[T - T_R] + a_4[T^2 - T_R^2] \quad (37)$$

$$B^{(1)}(T) = B^{(1)}(T_R) + a_5[T^1 - T_R^1] + a_6[\ln T - \ln T_R] + a_7[T - T_R] + a_8[T^2 - T_R^2] \quad (38)$$

$$C^*(T) = 0.0 \quad (39)$$

CaCl₂ (Phutela et al., 1987):

$$\begin{aligned} B^{(0)}(T) = a_1 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_2 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_3 \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) + \\ \left(T_R - \frac{T_R^2}{T} \right) B^{(0)L}(T_R) + B^{(0)}(T_R) \end{aligned} \quad (40)$$

$$B^{(1)}(T) = a_4 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + \left(T_R - \frac{T_R^2}{T} \right) B^{(1)L}(T_R) + B^{(1)}(T_R) \quad (41)$$

$$C^{\Phi}(T) = \left(T_R - \frac{T_R^2}{T} \right) C^{\Phi L}(T_R) + C^{\Phi}(T_R) \quad (42)$$

MgCl₂ (Phutela et al., 1987):

$$\begin{aligned} B^{(0)}(T) = a_1 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_2 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_3 \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) + \\ \left(T_R - \frac{T_R^2}{T} \right) B^{(0)L}(T_R) + B^{(0)}(T_R) \end{aligned} \quad (43)$$

$$\begin{aligned} B^{(1)}(T) = a_4 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_2 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_3 \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) \\ + \left(T_R - \frac{T_R^2}{T} \right) B^{(1)L}(T_R) + B^{(1)}(T_R) \end{aligned} \quad (44)$$

$$C^{\Phi}(T) = \left(T_R - \frac{T_R^2}{T} \right) C^{\Phi L}(T_R) + C^{\Phi}(T_R) \quad (45)$$

SrCl₂ (Phutela et al., 1987):

$$\begin{aligned} B^{(0)}(T) = a_1 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_2 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + \left(T_R - \frac{T_R^2}{T} \right) B^{(0)L}(T_R) + \\ B^{(0)}(T_R) \end{aligned} \quad (46)$$

$$\begin{aligned} B^{(1)}(T) = a_3 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_4 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + \left(T_R - \frac{T_R^2}{T} \right) B^{(1)L}(T_R) + \\ B^{(1)}(T_R) \end{aligned} \quad (47)$$

$$C^{\Phi}(T) = \left(T_R - \frac{T_R^2}{T} \right) C^{\Phi L}(T_R) + C^{\Phi}(T_R) \quad (48)$$

Na_2SO_4 (Holmes and Mesmer, 1986):

$$\begin{aligned} B^{(0)}(T) = & a_1 + a_2\left(T_R - \frac{T_R^2}{T}\right) + a_3\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) + a_4\left(\ln\frac{T}{T_R} + \frac{T_R}{T} - 1\right) \\ & + a_5\left(\frac{1}{680 - T} + \frac{T_R^2 - 680T}{T(680 - T_R)^2}\right) \end{aligned} \quad (49)$$

$$\begin{aligned} B^{(1)}(T) = & a_6 + a_7\left(T_R - \frac{T_R^2}{T}\right) + a_8\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) + a_9\left(T + \frac{T_R^2}{T} - 2T_R\right) \\ & + a_{10}\left(\ln\frac{T}{T_R} + \frac{T_R}{T} - 1\right) + a_{11}\left(\frac{1}{680 - T} + \frac{T_R^2 - 680T}{T(680 - T_R)^2}\right) \end{aligned} \quad (50)$$

$$\begin{aligned} C^*(T) = & a_{12} + a_{13}\left(T_R - \frac{T_R^2}{T}\right) + a_{14}\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) + a_{15}\left(T + \frac{T_R^2}{T} - 2T_R\right) \\ & + a_{16}\left(\ln\frac{T}{T_R} + \frac{T_R}{T} - 1\right) + a_{17}\left(\frac{1}{680 - T} + \frac{T_R^2 - 680T}{T(680 - T_R)^2}\right) \end{aligned} \quad (51)$$

K_2SO_4 (Holmes and Mesmer, 1986):

$$B^{(0)}(T) = a_1 + a_2\left(T_R - \frac{T_R^2}{T}\right) + a_3\left(T + \frac{T_R^2}{T} - 2T_R\right) + a_4\left(\ln\frac{T}{T_R} + \frac{T_R}{T} - 1\right) \quad (52)$$

$$\begin{aligned} B^{(1)}(T) = & a_5 + a_6\left(T_R - \frac{T_R^2}{T}\right) + a_7\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) + a_8\left(T - \frac{T_R^2}{T} - 2T_R\right) \\ & + a_9\left(\frac{1}{T - 263} + \frac{263T - T_R^2}{T(T_R - 263)^2}\right) \end{aligned} \quad (53)$$

$$C^*(T) = a_{10} + a_{11}\left(T + \frac{T_R^2}{T} - 2T_R\right) \quad (54)$$

Li_2SO_4 (Holmes and Mesmer, 1986):

$$B^{(0)}(T) = a_1 + a_2\left(T_R - \frac{T_R^2}{T}\right) + a_3\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) \quad (55)$$

$$\begin{aligned} B^{(1)}(T) = & a_4 + a_5\left(T_R - \frac{T_R^2}{T}\right) + a_6\left(\ln\frac{T}{T_R} + \frac{T_R}{T} - 1\right) + \\ & a_7\left(\frac{1}{680 - T} + \frac{T_R^2 - 680T}{T(680 - T_R)^2}\right) \end{aligned} \quad (56)$$

$$\begin{aligned} C^*(T) = & a_8 + a_9\left(T_R - \frac{T_R^2}{T}\right) + a_{10}\left(T^2 + \frac{2T_R^3}{T} - 3T_R^2\right) + \\ & a_{11}\left(\frac{1}{T - 263} + \frac{263T - T_R^2}{T(T_R - 263)^2}\right) \end{aligned} \quad (57)$$

Cs_2SO_4 (Holmes and Mesmer, 1986):

$$\begin{aligned} B^{(0)}(T) = & a_1 + a_2 \left(T_R - \frac{T_R^2}{T} \right) + a_3 \left(T^2 + \frac{2T_R^3}{T} - 3T_R^2 \right) + a_4 \left(T + \frac{T_R^2}{T} - 2T_R \right) + \\ & a_4 \left(\ln \frac{T}{T_R} + \frac{T_R}{T} - 1 \right) + a_6 \left(\frac{1}{T - 263} + \frac{263T - T_R^2}{T(T_R - 263)^2} \right) \end{aligned} \quad (57)$$

$$\begin{aligned} B^{(1)}(T) = & a_7 + a_8 \left(T_R - \frac{T_R^2}{T} \right) + a_9 \left(T^2 + \frac{2T_R^3}{T} - 3T_R^2 \right) + a_{10} \left(T + \frac{T_R^2}{T} - 2T_R \right) + \\ & a_{11} \left(\ln \frac{T}{T_R} + \frac{T_R}{T} - 1 \right) + a_{12} \left(\frac{1}{680 - T} + \frac{T_R^2 - 680T}{T(680 - T_R)^2} \right) \end{aligned} \quad (59)$$

$$C^*(T) = a_{13} + a_{13} \left(T_R - \frac{T_R^2}{T} \right) \quad (60)$$

MgSO_4 (Phutela and Pitzer, 1986):

$$\begin{aligned} B^{(0)}(T) = & a_1 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_2 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_3 \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) + \\ & a_4 \left(\frac{T^4}{20} + \frac{T_R^5}{5T} - \frac{T_R^4}{4} \right) + \left(T_R - \frac{T_R^2}{T} \right) B^{(0)L}(T_R) + B^{(0)}(T_R) \end{aligned} \quad (61)$$

$$\begin{aligned} B^{(1)}(T) = & a_5 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_6 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + \left(T_R - \frac{T_R^2}{T} \right) B^{(1)L}(T_R) + \\ & B^{(1)}(T_R) \end{aligned} \quad (62)$$

$$\begin{aligned} B^{(2)}(T) = & a_7 \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_8 \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_9 \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) + \\ & \left(T_R - \frac{T_R^2}{T} \right) B^{(2)L}(T_R) + B^{(2)}(T_R) \end{aligned} \quad (63)$$

$$\begin{aligned} C^*(T) = & a_{10} \left(\frac{T}{2} + \frac{T_R^2}{2T} - T_R \right) + a_{11} \left(\frac{T^2}{6} + \frac{T_R^3}{3T} - \frac{T_R^2}{2} \right) + a_{12} \left(\frac{T^3}{12} + \frac{T_R^4}{4T} - \frac{T_R^3}{3} \right) + \\ & a_{13} \left(\frac{T^4}{20} + \frac{T_R^5}{5T} - \frac{T_R^4}{4} \right) + \left(T_R - \frac{T_R^2}{T} \right) C^{*L}(T_R) + C^*(T_R) \end{aligned} \quad (64)$$

where:	a_i	= regression coefficient (values listed in the given references)
	T	= temperature of interest (K)
	T_R	= reference temperature (298.15K)
	$\beta^{(0)}(T)$	= the value of $\beta^{(0)}$ at the temperature of interest
	$\beta^{(1)}(T)$	= the value of $\beta^{(1)}$ at the temperature of interest
	$\beta^{(2)}(T)$	= the value of $\beta^{(2)}$ at the temperature of interest
	$C^*(T)$	= the value of C^* at the temperature of interest
	$\beta^{(0)}(T_R)$	= the value of $\beta^{(0)}$ at 298.15K
	$\beta^{(1)}(T_R)$	= the value of $\beta^{(1)}$ at 298.15K
	$\beta^{(2)}(T_R)$	= the value of $\beta^{(2)}$ at 298.15K
	$C^*(T_R)$	= the value of C^* at 298.15K
	$\beta^{(0)L}(T_R)$	= the apparent molar enthalpy of $\beta^{(0)}$ at 298.15K
	$\beta^{(1)L}(T_R)$	= the apparent molar enthalpy of $\beta^{(1)}$ at 298.15K
	$\beta^{(2)L}(T_R)$	= the apparent molar enthalpy of $\beta^{(2)}$ at 298.15K
	$C^{*L}(T_R)$	= the apparent molar enthalpy of C^* at 298.15K

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APPENDIX 5**USER'S GUIDES FOR THE COMPUTER CODES**

The following pages describe the information which must be supplied to the programs by the user of the model in order to undertake a simulation. The model actually consists of four programs:

STR.FUNC: calculates stream function values at all nodes in a two-dimension cross section, using the finite element method;

STR.LINE: contours the stream function values to determine the x- and y-coordinates along the stream lines, and calculates the groundwater velocities at all points along the stream line;

STR.TUBE: forms stream tubes from the flow lines and, divides flow tubes into a series of mixing cells;

MIX.REAC: transports mass by advection and dispersion through a two-dimensional cross section represented by a series of mixing cells and undertakes geochemical reactions in all cell.

There are several subscripted variables used in the programs which must be properly dimensioned. The following information provides the basis for dimensioning individual arrays for a given problem. In addition, this appendix provides the user with a list of the input variables, their definitions, and the order and format that the variables must be entered.

STR.FUNC: Dimensioning the Arrays

```

REAL*8 S(nnodee,nb), SC(nnodee,nhead), SFVAL(nnodee), F(nnodee), KX(nelme),
      KZ(nelme), CHEAD(nhead), VX(nhelm,nvelm), VZ(nhelm,nvelm)
REAL POR(nunit), KHORZ(nunit), KVERT(nunit), X(nnodee), Z(nnodee),
      CHVAL(nrow,ncol), FLUX(nrow,ncol), FB(nnodee), VELDIR(nhelm,nvelm)
INTEGER*2 IDBBR(ncol), IDWTR(ncol), MAPGEO(nhelm,nvcell), LC(nnodee), IN(nelme,3),
      II(100), JJ(100)
LOGICAL*1 TYPE(nnodee), IC(8)
CHARACTER*80 TITLE

```

where: nnodee = estimated number of nodes in the grid
 nelme = estimated number of elements in the grid
 ncol = number of columns of nodes
 nrow = number of rows of nodes
 nhead = number of constant head nodes
 nvcell = number of cells (ncol - 1)
 nhelm = number of horizontal elements (nrow - 1)
 nvelm = number of vertical elements (ncol x 2 - 1)
 nunit = number of hydrostratigraphic units

STR.FUNC: Input Variables

TITLE : any title up to 80 characters
 IC : program control parameters;
 IC(1): calculate the stream function values
 IC(2): print the node coordinates
 IC(3): print the element incidences
 IC(4): print the stream function values
 IC(5): output stream function values to a disk file
 IC(6): calculate the velocity field
 IC(7): print the velocity field
 NROW : number of rows of nodes in the grid
 NCOL : number of columns of nodes in the grid
 NCHEAD : number of constant head nodes
 NGEOL : number of hydrostratigraphic units
 NFLUX : number of pre-defined flux nodes
 DELX : horizontal node spacing
 DELZ : vertical node spacing
 ANGLE : angle of inclination of K_h and K_v from the coordinate axes
 IDWTR : code to indicate which rows mark the water table
 IDBBR : code to indicate which rows mark the lower boundary of the flow domain
 II : column indicator for a node assigned a value of CHVAL or FLUX
 JJ : row indicator for a node assigned a value of CHVAL or FLUX
 CHVAL : constant head values assigned to nodes
 FLUX : flux values assigned to nodes
 KHORZ : horizontal hydraulic conductivity assigned to the hydrostratigraphic units
 KVERT : vertical hydraulic conductivity assigned to the hydrostratigraphic units
 POR : porosity assigned to the hydrostratigraphic units
 MAPGEO : code to define the hydrostratigraphic units

STR.FUNC: Formats for the Input Variables

LINE 1:	TITLE	A80
LINE 2:	IC	8L2
LINE 3:	NROW,NCOL,NCHEAD,NGEOL,NFLUX	5I5
LINE 4:	DELX,DELZ,ANGLE	3F10.0
LINE 5: ¹	IDWTR	25I3
LINE 6: ¹	IDBBR	25I3
LINE 7: ¹	II,JJ,CHVAL	6(2I3,F6.0)
LINE 8: ¹	II,JJ,FLUX	6(2I3,F6.0)
LINE 9: ²	I,KHORZ,KVERT,POR	I5,3E10.5
LINE 10: ³	MAPGEO	80I1

1: continue with as many lines as needed to include all required values

2: continue with one line for each hydrostratigraphic unit

3: continue with one line for each for each row in the grid

STR.LINE: Dimensioning the Arrays

```
REAL    CVAL(nlines), SFVALS(ncol,nrow), SFVAL(nnodee), XU(4), YU(4), XL(4), YL(4)
INTEGER IOP(8)
```

where: nnodee = estimated number of nodes in the grid
 ncol = number of columns of nodes
 nrow = number of rows of nodes
 nlines = number of stream lines

STR.LINE: Input Variables

TITLE : any title up to 80 characters
 NROW : number of rows of nodes in the grid
 NCOL : number of columns of nodes in the grid
 NCNTR : number of stream lines
 CVAL : values of the stream functions used to contour the stream lines
 SFVAL : number of stream function values from the program STR.FUNC
 IOPT : code to determine if the mixing cells should be plotted
 NTUBE : number of stream tubes
 NTUBE : identifying number for a stream tube
 NCELL : number of mixing cells in a stream tube
 XU : x-coordinates defining the upper boundary of a mixing cell
 YU : y-coordinates defining the upper boundary of a mixing cell
 XL : x-coordinates defining the lower boundary of a mixing cell
 YL : y-coordinates defining the lower boundary of a mixing cell

STR.LINE: Formats for the Input Variables

LINE 1:	TITLE	A80
LINE 2:	IOP	8L2
LINE 3:	NCNTR,NROW,NCOL	3I5
LINE 4: ¹	CVAL	8F10.0
LINE 5: ¹	I,SFVAL	4(I5,E13.5)
LINE 6:	IOPT	I5
LINE 7: ²	NTUBE,NOTUBE,NCELL	3I5
LINE 8: ²	XU,YU	8F10.0
LINE 9: ²	XL,YL	8F10.0

1: continue with as many lines as needed to include all required values
 2: continue with one group of these three lines for each stream tube

STR.TUBE: Dimensioning the Arrays

```

REAL*8  AREA(ncell), SBAREA(3), VELL(npts), VELU(npts)
REAL*4  XCNT(3,npts), YCNT(3,npts), XCNTL(npts), YCNTL(npts), XCNTU(npts),
        YCNTU(npts), CVAL(3), LXBND(ncell), LYBND(ncell), LTBND(ncell),
        UTBND(ncell), UXBND(ncell), UYBND(ncell)
INTEGER NPTS(3)

```

where: npts = estimated number of points along a flow line
ncell = estimated number of mixing cells in a stream tube

STR.TUBE: Input Variables

TITLE : any title up to 80 characters
NTUBE : number of stream tubes
NPMAX : estimated maximum number of points along the stream tubes
DELT : size of the time step
NPTS : number of points along a stream line
CVAL : stream function values of the stream line
XCNT : x-coordinate of the points along a stream line
YCNT : y-coordinate of the points along a stream line

STR.TUBE: Formats for the Input Variables

LINE 1:	TITLE	A80
LINE 2:	NTUBE,NPMAX,DELT	2I5,F10.0
LINE 4: ^{1,2}	NPTS,CVAL	I10,F10.0
LINE 5: ^{3,1,2}	XCNT,YCNT	2E15.5

- 1: continue with 1 pair of LINES 4 and 5 for each stream tube boundary
- 2: continue with 3 stream lines for each stream tube boundary
- 3: continue with 1 line for each point along a stream line

MIX.REAC: Dimensioning the Arrays

```

REAL*8  LM(nspec), M(nspec), LA(nspec), LG(nspec), LKSP(nspec), DM2(nspec),
        TOT(neq), DELTA(neq), DELTOT(neq), AR(neq,neq), AS(neq,neq), CR(neq),
        AREA(ncell), LKMIN(nmin), TOTAL(2,neq), DIFFZ(2), DTOT(ncomp),
        DHLOOK(nmin), CR(neq)
REAL*4  XL(ncell,8), YL(ncell,8), XU(ncell,8), YU(ncell,8), AREA(ncell), DIF(ncell,nspec),
        DHA(nspec), MOLSPE(nspec), CONC(ncell,nspec), CONCI(nspec), SAT(ncell),
        MASSF(ncell,nspec), ALKSP(nspec), MASSD(ncell,nspec), MASSR(ncell,nspec),
        MASSA(ncell,nspec), MOLALE(ncell,nspec), MOLALR(ncell,nspec),
        CONCR(ncell,nspec), MASH2O(ncell), CSP(nspec,6), ZSP(nspec), THSP(nspec),
        DHSP(nspec), LKOSP(nspec), ASP(nspec,5), SDENS(2), ADHSP(nspec,2),
        TH(2), TEMP(2), SIMIN(nmin), CMIN(nmin,10), THMIN(nmin), ALOOK(nmin,5),
        CLOOK(nmin,10), LKTO(nmin), DHMIN(nmin), AMIN(nmin,5), TMIN(nmin),
        CMCON(nmin,5), CMINO(nmin,10), LKMINO(nmin), XSTEP(nstep), TSTEP(nstep),
        CREAC(nreacc), GFW(ncomp), THMEAN(nreacc)
INTEGER*2 NSP(nspec), LSP(nspec,6), KFLAG(nspec), IGFLAG(nspec), ISFLAG(nspec),
        IIN(ncomp), IOUT(ncomp), ISOLV(2), NMIN(nmin), LMIN(nmin,10),
        MFLAG(nmin), LMCON(nmin,5), NMCON(nmin), LMINO(nmin,10), NMINO(nmin),
        IOPT(10), IALK(2), IUNITS(2), NSUM(nsum), LSUM(nsum), LREAC(nreacc),
        NLOOK(nmin), LKOLK(nmin), LOOKFL(nmin), LLOOK(nmin,10),
        LKLOOK(nmin), LT(nmin), ISUB(12), NUMPTZ(nspec)
CHARACTER*8 ELNAME(ncomp), MINAME(nmin), SPNAME(nspec), SUNAME(nsum),
        NAMELK(nmin), SUBS(12), TITLE(10), HEAD(2,10), CARD(10)

```

where: nspec = number of species in the groundwater regime
 ncell = estimated maximum number of mixing cells in a stream tube
 nmin = number of minerals in the geochemical data base
 nstep = number of reaction steps
 ncomp = number of components in the data base
 nreacc = number of components in a reaction
 neq = estimated number of mixing cells in a stream tube
 nsum = number of species in a sum of species

MIX.REAC: Input Variables and their Formats (mixing cell parameters)

TITLE : any title up to 80 characters
 NTUBE : number of stream tubes
 NPMAX : estimated maximum number of points along the stream tubes
 DELT : size of the time step
 NPTS : number of points along a stream line
 CVAL : stream function values of the stream line
 XCNT : x-coordinate of the points along a stream line
 YCNT : y-coordinate of the points along a stream line

Formats:

LINE 1:	TITLE	A80
LINE 2:	NTUBE,NPMAX,DELT	2I5,F10.0
LINE 4:1,2	NPTS,CVAL	I10,F10.0
LINE 5:1,2	XCNT,YCNT	2E15.5

1: continue with 1 pair of LINES 4 and 5 for each stream tube boundary
 2: continue with 3 stream lines for each stream tube boundary

MIX.REAC: Input Variables and their Formats (geochemical parameters)

The geochemical code is based on the program *PHREEQE* (Parkhurst et. al., 1980). The reader should refer to this publication for a complete description of the input parameters.

variables:

TITLE : any title up to 80 characters
 IOPT : program control options
 NSTEPS : number of reaction steps
 NCOMPS : number of constituents in a net stoichiometric reaction
 V0 : initial volume of solution 1 when modelling a titration

formats:

LINE 1: TITLE 20A4
 LINE 2: (IOPT(l),l=1,9),NSTEPS,NCOMPS,V0 9I1,1X,2I2,6X,F10.5

variables:

ELEMENTS : keyword indicating that these data are part of the element block of data
 TNAME : name of the element
 NELT : index number of the element
 TGFW : total gram formula weight of the element

formats:

LINE 1: ELEMENTS 'ELEMENTS'
 LINE 2:¹ TNAME,NELT,TGFW A8,I4,F13.0
 LINE 3: blank line

¹: LINE 2 is repeated for each element

variables:

SPECIES : keyword indicating that these data are part of the species block of data
 I : index number of the species
 SNAME : name of the species
 NSP : total number of elements in the association reaction that form the species
 KFLAG : code to indicate whether the van't Hoff expression or a regression function is used to calculate high temperature values of $\log(K_{eq})$
 ZSP : charge of the aqueous species
 THSP : sum of the operational valences of the redox species
 ALKSP : alkalinity of the species
 PITZNO : index number of the species in the Pitzer equation data base
 LKTOSP : $\log(K_{eq})$ at 25°C of the association reaction for the species
 DHSP : standard enthalpy of the association reaction at 25°C
 ASP : regression coefficients for a high temperature function for $\log(K_{eq})$
 LSP : element numbers of the components the elements forming the species
 CSP : stoichiometric coefficients for the elements forming the aqueous species

formats:

LINE 1:	SPECIES	'SPECIES'
LINE 2: ¹	I	I3
LINE 3: ¹	SNAME,NSP,KFLAG,ZSP,THSP,ALKSP,PITZNO	A8,I3,I1,2X,2F10.0, 30X,F10.0,I5
LINE 4: ^{1,2}	LKTOSP,DHSP,(ASP(I),I=1,5)	2F10.0,5E12.5
LINE 5: ¹	(LSP(I),CSP(I),I=1,NSP)	6(I3,F7.0)
LINE 6: ¹	blank line	

¹: continue with 1 group of LINES 2 to 6 for each species

²: values of ASP required only if KFLAG = 1

variables:

SOLUTION : keyword indicating that these data are part of the solution block of data
 TITLE : solution identifier
 SNAME : name of the species
 NTOTS : total number of elements and their concentrations in the solution
 IALK : code to indicate how total alkalinity is defined
 IUNITS : input units of concentration (mg/L, mol, ppm)
 PH : approximate pH of the solution
 PE : approximate pe of the solution
 TEMP : temperature of the solution (°C)
 SDENS : approximate density of the solution
 LT : index number of the element in the solution
 DTOT : concentration of the element in the solution

formats:

LINE 1: ¹	SOLUTION	'SOLUTION'
LINE 2: ¹	TITLE	20A4
LINE 3: ¹	NTOTS,IALK,IUNITS,PH,PE,TEMP,SDENS	I2,I3,I2,3X,4F10.0
LINE 4: ^{1,2}	(LT(I),DTOT(I),I=1,NTOTS)	5(I4,E11.3)

¹: continue with 1 group of LINES 1 to 4 for each mixing cell

²: continue with as many lines as necessary to include all elements

variables:

MINERALS	: keyword indicating that these data are part of the minerals block of data
MNAME	: name of the mineral to be equilibrated with the solution
NMINO	: number of species in the dissociation reaction of the mineral
THMIN	: sum of OPV's of the species in the dissociation reaction of the mineral
LKTOM	: $\log(K_{eq})$ of the dissociation reaction of the mineral
DHMIN	: standard enthalpy of the dissociation reaction of the mineral at 25°C
MFLAG	: code to indicate if the van't Hoff expression or a regression function is used to calculate the high temperature $\log(K_{eq})$
SIMIN	: saturation index of the mineral in the solution at equilibrium
LMIN	: index number of the species comprising the mineral dissociation reaction
CMIN	: stoichiometric coefficients of species in the mineral dissociation reaction
AMIN	: regression coefficients for the high temperature function for $\log(K_{eq})$

formats:

LINE 1: ¹	MINERALS	'MINERALS'
LINE 2: ¹	MNAME,NMINO,THMIN,LKTOM,DHMIN,MFLAG,SIMIN	A8,I4,3X, 3F10.0,I6,F19.0
LINE 3: ^{1,2}	(LMIN(I),CMIN(I),I=1,NMINO)	5(I4,F11.4)
LINE 4: ^{1,3}	(AMIN(I),I=1,5)	5E12.5
LINE 5: ¹	blank line	

¹: continue with 1 group of LINES 1 to 5 for each mineral in each mixing cell

²: continue with as many lines as necessary to include all elements

³: required only if MFLAG = 1

variables:

STEPS	: keyword to indicate that the following data relate to the steps of an optional reaction occurring within each cell
XSTEP	: reaction increments as defined by IOPT

formats:

LINE 1:1.2	STEPS	'STEPS'
LINE 2:2	(XSTEP(),I=1,NSTEPS)	8F10.3

¹: optional input
²: continue with LINES 1 and 2 for each mixing cell

variables:

REACTION : keyword indicating that these data relate to the stoichiometry and valences of elements added as a reaction

LREAC : index number of elements used in the reaction

CREAC : stoichiometric coefficients of the elements in the reactions

THMEAN : the OPV of the elements in the reaction

formats:

LINE 1: ^{1,2}	REACTION	'REACTION'
LINE 2: ²	(LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)	4(14,2F8,3)

¹: optional input
²: continue with LINES 1 and 2 for each mixing cell

variables:

NEUTRAL : keyword indicating that these data relate to the elements used to adjust the electrical neutrality of a solution (except H^+ , e^-)

LPOS : element number of the cation to add +ve charge to maintain a balance

LNEG : element number of the anion to add -ve charge to maintain a balance

formats:

LINE 1: ^{1,2}	NEUTRAL	'NEUTRAL'
LINE 2: ²	LPOS,LNEG	215

¹: optional input
²: continue with LINES 1 and 2 for each mixing cell

variable:

END : keyword used to mark the end of the geochemical input

format:

LINE 1:1 END 'END'

¹: continue with LINES 1 and 2 for each mixing cell

The variables listed on the following pages refer to the ion interaction parameters required by the Pitzer equations. All these parameters are contained within a separate data base. The species represented by these ion interaction parameters are listed in Table A.1.

variable:

NCION : number of cations in the Pitzer equation data base
 NAION : number of anions in the Pitzer equation data base
 NNEUT : number of neutral species in the Pitzer equation data base
 CHARGC : charge of the cation in the data base
 NAMEC : name of the cation in the data base
 CHARGA : charge of the anion in the data base
 NAMEA : name of the anion in the data base
 CHARGN : charge of the neutral species in the data base
 NAMEN : name of the neutral species in the data base

format:

LINE 1: NCION,NAION,NNEUT 3I10
 LINE 2:¹ (CHARGC(I),NAMEC(I),I=1,NCION) 8(I2,A8)
 LINE 3:¹ (CHARGA(I),NAMEA(I),I=1,NAION) 8(I2,A8)
 LINE 4:¹ (CHARGN(I),NAMEN(I),I=1,NNEUT) 8(' 0',A8)

¹: continue with as many lines as needed for all ions within each group

variable:

NAME : keyword to indicate that these data are $\beta^{(0)}$ values
 BETA0 : values of $\beta^{(0)}$ for cation - anion interactions

format:

LINE 1: NAME 'BETA(0)'
 LINE 2:^{1,2} (BETA0(IONC,IONA),IONA=1,NAION) 8F10.5

¹: continue with as many lines as required for the $\beta^{(0)}$'s for all anions in the data base corresponding to a single cation

²: continue with as many new lines as required for all cations

variable:

NAME : keyword to indicate that these data are $B^{(1)}$ values
 BETA1 : values of $B^{(1)}$ for cation - anion interactions

format:

LINE 1: NAME 'BETA(1)'
 LINE 2:^{1,2} (BETA1(IONC,IONA),IONA=1,NAION) 8F10.5

¹: continue with as many lines as required for the $B^{(1)}$'s for all anions in the data base corresponding to a single cation

²: continue with as many new lines as required for all cations

variable:

NAME : keyword to indicate that these data are $B^{(2)}$ values
 BETA2 : values of $B^{(2)}$ for cation - anion interactions

format:

LINE 1: NAME 'BETA(2)'
 LINE 2:^{1,2} (BETA2(IONC,IONA),IONA=1,NAION) 8F10.5

¹: continue with as many lines as required for the $B^{(2)}$'s for all anions in the data base corresponding to a single cation

²: continue with as many new lines as required for all cations

variable:

NAME : keyword to indicate that these data are $C^{(*)}$ values
 CPHI : values of $C^{(*)}$ for cation - anion interactions

format:

LINE 1: NAME 'C(PHI)'
 LINE 2:^{1,2} (CPHI(IONC,IONA),IONA=1,NAION) 8F10.5

¹: continue with as many lines as required for the $C^{(*)}$'s for all anions in the data base corresponding to a single cation

²: continue with as many new lines as required for all cations

variable:

NAME : keyword to indicate that these data are θ_{cc} values
 THETAC : values of θ_{cc} for cation - cation interactions

format:

LINE 1: NAME 'THETA(cat)'
 LINE 2:^{1,2} (THETAC(ION1,ION2),ION2=1,NCION) 8F10.5

- ¹: continue with as many lines as required for the θ_{cc} 's for all cations in the data base corresponding to a single cation
²: continue with as many new lines as required for all cations

variable:

NAME : keyword to indicate that these data are θ_{aa} values
 THETAA : values of θ_{aa} for anion - anion interactions

format:

LINE 1: NAME 'THETA(an)'
 LINE 2:^{1,2} (THETAA(ION1,ION2),ION2=1,NAION) 8F10.5

- ¹: continue with as many lines as required for the θ_{aa} 's for all anions in the data base corresponding to a single anion
²: continue with as many new lines as required for all anions

variable:

NAME : keyword to indicate that these data are ψ_{cca} values
 NPSION : number of values of ψ_{cca} in the data base
 ION1 : identification number of the first cation in the triple ion interaction
 ION2 : identification number of the second cation in the triple ion interaction
 PSIC : values of ψ_{cca} for cation - cation - anion interactions

format:

LINE 1: NAME,NPSION 'PSI(c-c-a)',I5
 LINE 2:¹ ION1,ION2,(PSIC(ION1,ION2,IONC),IONC=1,7) 2I5,7F10.5
 LINE 3:^{1,2} (PSIC(ION1,ION2,IONC),IONC=18,NCION) 8F10.5

- ¹: continue with as many new LINES 2 and 3 as required for all values of ψ_{cca}
²: continue with as many lines 3 as required for values of ψ_{cca} for anions numbered 8 or greater for a specific cation - cation pair
-

variable:

NAME : keyword to indicate that these data are ψ_{ac} values
 NPSION : number of values of ψ_{ac} in the data base
 ION1 : identification number of the first anion in the triple ion interaction
 ION2 : identification number of the second anion in the triple ion interaction
 PSIA : values of ψ_{ac} for anion - anion - cation interactions

format:

LINE 1: NAME,NPSION 'PSI(a-a-c)',I5
 LINE 2:¹ ION1,ION2,(PSIA(ION1,ION2,IONA),IONA=1,7) 2I5,7F10.5
 LINE 3:^{1,2} (PSIA(ION1,ION2,IONA),IONA=8,NAION) 8F10.5

- ¹: continue with as many new LINES 2 and 3 as required for values of ψ_{ac}
²: continue with as many lines 3 as required for values of ψ_{ac} for cations numbered 8 or greater for a specific anion - anion pair

variable:

NAME : keyword to indicate that these data are λ_{nc} values
 LAMDAC : values of λ_{nc} for neutral species - cation interactions

format:

LINE 1: NAME 'LAMBDA(n,c)'
 LINE 2:^{1,2} (LAMDAC(IONN,IONC),IONC=1,NCION) 8F10.5

- ¹: continue with as many lines as required for the λ_{nc} 's for all cations in the data base corresponding to a single neutral species
²: continue with as many new lines as required for all neutral species

variable:

NAME : keyword to indicate that these data are λ_{na} values
 LAMDAA : values of λ_{na} for neutral species - anion interactions

format:

LINE 1: NAME 'LAMBDA(n,a)'
 LINE 2:^{1,2} (LAMDAA(IONN,IONA),IONA=1,NAION) 8F10.5

- ¹: continue with as many lines as required for the λ_{na} 's for all anions in the data base corresponding to a single neutral species
²: continue with as many new lines as required for all neutral species
-

variable:

NAME : keyword to indicate that these data are temperature regression coefficients for $B^{(0)}$, $B^{(1)}$, $B^{(2)}$ and $C^{(*)}$
 NREG : number of cation - anion interaction parameters which have temperature regression coefficients
 IONC : identification number of cation
 IONA : identification number of anion
 BETA0C : values of the temperature regression coefficients for $B^{(0)}$
 BETA1C : values of the temperature regression coefficients for $B^{(1)}$
 BETA2C : values of the temperature regression coefficients for $B^{(2)}$
 CPHIC : values of the temperature regression coefficients for $C^{(*)}$

format:

LINE 1:	NAME,NREG	TEMP REG. 'J5
LINE 2: ¹	IONC, IONA, (BETA0C(IONC,IONA,K),K=1,4)	2I5,4E15.5
LINE 3: ¹	(BETA1C(IONC,IONA,K),K=1,4)	10X,4E15.5
LINE 4: ¹	(BETA2C(IONC,IONA,K),K=1,4)	10X,4E15.5
LINE 5: ¹	(CPHIC(IONC,IONA,K),K=1,4)	10X,4E15.5

¹: continue with as many lines 2 to 5 as required for cation -anion interaction parameters which have temperature regression coefficients

APPENDIX 6

Computer programs, data bases
and example input and output
for simulations (in pocket)

APPENDIX WAS NOT MICROFILMED.
PLEASE REFER, IF NEED BE, TO THE
ORIGINAL THESIS DEPOSITED IN THE
UNIVERSITY CONFERRING THE
DEGREE.

L'APPENDICE N'A PAS ETE MICROFILME.
VEUILLEZ VOUS REFERER AU BESOIN A LA
THESE ORIGINALE DEPOSEE A
L'UNIVERSITE QUI A CONFERE LE
GRADE.